



Release of silver and titanium from face masks traded for the general population

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ABSTRACT

Previous assessments of a selection of face masks intended for the general population in Belgium found that silver (Ag)-based biocides were present in masks advertised for antimicrobial properties; whereas titanium dioxide (TiO₂) particles were detected in all the face masks in at least one layer corroborating its widespread use in the textile industry. The presence of Ag-based biocides and TiO₂ particles in face masks raised questions on the possibility of release under normal wearing conditions, which could potentially cause a health risk to the consumers. Direct measurement of release of Ag and TiO₂ particles during normal wearing is problematic by the lack of methodology to test release and to quantify inhaled particles. Therefore in this study, we investigated leaching experiments using artificial acid sweat as a method to evaluate the release of Ag-based biocides and TiO₂ particles present in face masks. Leaching experiments were proposed as an alternative method to evaluate the quality of face masks, and as a higher tier method to assess face masks that are not safe-by-design. Results from leaching experiments showed that Ag was released in amounts varying from 0.03 up to 36 % of total Ag content, in four out of the eight face masks that claimed antimicrobial properties and that contained Ag. The leaching data of titanium (Ti) showed that despite TiO₂ being detected in all face masks, only in one mask Ti was measured in detectable concentrations in artificial sweat (0.35 % of total Ti content). Comparison of leachable Ag and Ti with respective acceptable exposure limit values derived from inhalation exposure limits indicate that three face masks would need further risk assessment and could not be considered as intrinsically safe.

1. Introduction

During the COVID-19 crisis the demand of face masks increased rapidly and due to shortages of medical face masks, single-use and reusable face masks made from various materials were brought to the market. Also, textiles functionalized with nanoparticles were used for the production of face masks for their alleged positive effects of improved breathability, higher filtration capacity, or antiviral and antimicrobial properties (Chua et al., 2020; Palmieri et al., 2021). Masks of a so-called improved performance were sold for the general population without proper verification of such claims. Antibacterial and antiviral properties were the main claims of face masks towards coronavirus disease prevention, though in many cases such claims were not supported (Blevens et al., 2021).

Metals, including silver (Ag) and copper (Cu) and nanoparticles of metal oxides, including zinc oxide (ZnO), copper oxide (CuO), and titanium dioxide (TiO₂) have been used for the production of textiles with

antimicrobial or other functional finishing properties (Bhandari et al., 2022). The attributed modes of actions for observed biocidal effects include the generation of reactive oxygen species, damage to cellular proteins and lipids, and inhibition of DNA and RNA synthesis (Almeida and Ramos, 2017; Morais et al., 2016). Among the nanoparticles, TiO₂ further received attention in the textile industry because of its various other applications when incorporated on textiles, such as to provide UV-protection, self-cleaning, hydrophobicity, wrinkle resistance (Montazer and Pakdel, 2011; Rashid et al., 2021).

An important challenge of functionalizing textiles with nanoparticles is that their poor adhesion to the fibre can result in leaching of the nanoparticles by laundering or rubbing (Bhandari et al., 2022). Indeed, health concerns regarding the application of textiles functionalized with nanoparticles are sustained in a number of studies that showed their potential release in experimental conditions that simulate normal wearing and/or washing (Quadros et al., 2013; von Goetz et al., 2013). However, to date, there is no standard method to evaluate leaching of

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metal nanoparticles from functionalized textiles. Variations (Herrero et al., 2019; Suwanroek et al., 2022; Wagener et al., 2016) to the method proposed by von Goetz et al. (2013) which includes chemical (simulants) and physical stresses (abrasion), have been used to evaluate release of chemical substances including nanoparticles from textiles. Often synthetic human sweat has been used as leaching solution considering that textiles are in contact with the skin. Three standard protocols, the European Standard EN 1811 (pH 6.5) (CEN, 2011), the ISO 105-E04 (pH 5.5 and pH 8.0) (ISO, 2013) and the AATCC test method TM015 (pH 4.3) (AATCC, 2013) have been used to prepare artificial human sweat in migration experiments (Hedberg et al., 2014; Kulthong et al., 2010; von Goetz et al., 2013). An advantage of leaching experiments is that they are relatively cheap and easy to conduct under normal laboratory conditions.

As various functionalized textiles are used for face mask production, it is necessary to evaluate the quality of the face masks and the potential risks to which the wearers are exposed when chemicals, including nanoparticles are released. Hereto, leaching methods can be useful to characterize the release of chemicals from face masks during wearing. Only a limited number of published studies have investigated release of metals from face masks. For example, Suwanroek et al. (2022) investigated the release of Zn in water or detergent from fabric face masks that were labelled to contain ZnO nanocomposites as an antimicrobial agent. In this study, release of Zn was low (up to 3 % of total Zn) which was explained by the in situ nanoparticle deposition method that was applied as functionalization technology of the fabric (Suwanroek et al., 2022). Pollard et al. (2021) evaluated the release of Ag and Cu in various leaching solutions (deionized water, detergent, artificial saliva) from nine face masks with claimed antimicrobial properties. The amounts of Ag and Cu that leached out varied strongly between the face masks and conditions. In general, higher release was observed with the detergent solution and Cu appeared to migrate more easily than Ag under the investigated experimental conditions (Pollard et al., 2021).

An assessment on a selection of face masks available on the Belgian market showed that 13 of the 20 investigated masks contained Ag-based biocides including Ag⁺ ions or Ag⁰ nanoparticles in the textile fibres (Mast et al., 2023), while TiO₂ particles were detected in almost all layers containing synthetic fibres (Verleysen et al., 2022). The presence of Ag-based biocides and TiO₂ particles in face masks raised questions on the possibility of release under normal wearing conditions and on the potential resulting health risks for the wearers. Direct measurement of the release of Ag-based biocides and TiO₂ nanoparticles during normal wearing is problematic by methodological limitations to test release and to quantify inhaled particles. Therefore, in this work we considered leaching experiments as a method to evaluate the release of Ag-based biocides and TiO₂ particles present in face masks, and we evaluated if leaching data can be used as a higher tier method to refine risk assessment for Ag (Mast et al., 2023) and TiO₂ (Verleysen et al., 2022) for face masks that are not safe-by-design.

2. Materials and methods

2.1. Chemicals

All salts used in the experiment were of analytical reagent grade. Sodium chloride (NaCl) was purchased from VWR, sodium dihydrogen orthophosphate dihydrate (NaH₂PO₄·2H₂O) Emprove® Essential from Sigma-Aldrich, L-histidine monohydrochloride monohydrate (C₆H₉O₂N₃·HCl·H₂O) from Sigma-Aldrich. Sodium hydroxide (NaOH) 1 M solution was from Honeywell's Fluka chemicals and nitric acid (HNO₃, 67–69 % w/w, pico-pure) from ChemLab. Single element ICP-MS standard solutions were from CPACHEM (Ag, 1000 mg/L in 2 % HNO₃ and Ti, 1000 mg/L in 5 % HNO₃ and 0.5 % hydrofluoric acid HF). In-house double-distilled water (1.0–1.5 µS/cm) was used for all chemical analysis and preparation of solutions.

2.2. Selection of face masks for migration experiments

The ten face masks used in the present study were commercially available in Belgium and EU market and were purchased in 2021. The masks were intended to protect the general population against the spread of COVID-19 disease. The selection of face masks included single use and reusable masks made from a variety of materials, including cotton, non-woven fabric, polyester and polyamide. Total amounts of Ti and Ag present in the face masks were previously determined after acid digestion and ranged from a non-detectable amount up to 235044 µg Ag per mask (Mast et al., 2023) and from 11 µg up to 152345 µg TiO₂ per mask (Verleysen et al., 2022) (Table 1).

2.3. Leaching of Ag and Ti in artificial acid sweat solution

Artificial acid sweat solution used in the leaching experiments was prepared following the protocol described in the ISO procedure 105-E04 for 'colour fastness to perspiration' (ISO, 2013). Briefly, 5 g of sodium chloride, 2.2 g of sodium dihydrogen orthophosphate dihydrate and 0.5 g of L-histidine monohydrochloride monohydrate were dissolved in 1000 mL of bi-distilled water. The solution was brought to pH 5.5 (±0.2) with a solution 0.1 M NaOH.

Prior to cutting pieces of face mask for the leaching experiment, the weight of the whole face mask was recorded after removing the metal nose clips (if present) and the ear loops. For masks that contained different layers, the layers were separated and weighed. For the migration experiment a piece of face mask (6 cm × 6 cm) was cut, accurately weighed and placed in a 50 mL polypropylene tube. Then, 20 mL of preheated (37 °C) freshly prepared artificial acid sweat was added to each tube. The tubes were screw tightened with a lid and agitated at a speed of approximately 57 rpm in an overhead shaker (Heidolph Reax 2) that was placed in a pre-heated (37 °C) incubator. The size of the piece of mask was selected such that it is representative for the entire mask while the size of the sample allows fitting it in the plastic tubes allowing full contact with the artificial sweat solution. Depending on the size of the mask, the size of 6 cm × 6 cm represented 25–50 % of the entire mask. An exception was mask AgMask 18 (elastane mask) and AgMask 20 (nanofiber filter) for which the 6 cm × 6 cm corresponded to almost the entire mask. The same solid-to-liquid ratio of 1.8 (area:volume) was

Table 1
Overview of the selected face masks used in the leaching experiments.

Face mask	Ag (µg/mask) ^a	TiO ₂ (µg/mask) ^a	Type of mask	Form of Ag biocide
AgMask-05	N.D.	791	Single use	
AgMask-11	N.D.	11	Single use	
AgMask-20	6.5	2298	Reusable	Ag ⁺ ions
AgMask-12	7.3	8175	Single use	Ag ⁺ ions
AgMask-13	13	12196	Reusable	Ag ⁺ ions
AgMask-03	37	30752	Reusable	Ag ⁺ ions, nanoparticles and large Ag ⁰ particles
AgMask-14	87	29	Reusable	Ag ⁺ ions
AgMask-15	165	152345	Reusable	Ag ⁰ nanoparticles
AgMask-18	176	19146	Reusable	Ag ⁺ ions
AgMask-08	235044	12297	Reusable	Ag ⁺ ions, Ag ⁰ nanoparticles, Ag ⁰ coating

N.D.: not detected.

^a Total content of Ag and TiO₂ in the mask was determined by ICP-MS and ICP-OES after microwave digestion in concentrated acid, from Mast et al. (2023) and Verleysen et al. (2022).

assured for all samples.

After contact times of 1, 4, 8 and 24 h, the pieces of face mask were removed from the tubes. Next, 1 mL of the supernatant leachate solution was subsampled and acidified to 4 % v/v HNO₃ using concentrated HNO₃. Control blank samples (without face mask) and spiked blank samples containing Ag 100 µg/L and Ti 10 µg/L were also measured in the experiment as controls. All migration experiments were conducted in duplicate. For face masks that were composed of layers with distinctive fabrics or elemental contents (i.e. AgMask-03, AgMask-08, AgMask-13, AgMask-14, AgMask-18, AgMask-20), the leaching experiment was conducted on each separate layer.

2.4. Analysis of Ag and Ti

Leached Ag and Ti concentrations were measured by triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS, Agilent 8800). Silver was analysed on-mass (m/z 107–107) in the helium (He) collision cell mode and Ti was measured in mass-shift mode (m/z 48–64) using a mixture of oxygen (O₂) and hydrogen (H₂) reaction cell gases to resolve isobaric (mainly ⁴⁸Ca) and polyatomic interferences (e.g. ³¹P¹⁶O¹H⁺). As described by Noireaux et al. (2021) Q1 was set to m/z 48, the mass of the precursor ⁴⁸Ti⁺ ion and Q2 was set to m/z 64, the mass of the target product ion ⁴⁸Ti¹⁶O⁺. Addition of H₂ promoted formation of ⁴⁸Ca¹⁶O¹H⁺, avoiding interference of ⁴⁸Ca¹⁶O⁺ on ⁴⁸Ti¹⁶O⁺. An internal standard solution containing scandium (Sc) and indium (In) at a concentration of 200 µg/L was added online to correct for measurement drift. Matrix-matched calibration standards were prepared using certified single element standard solutions (1000 mg/L). All solutions were acidified with concentrated HNO₃. Estimation of the limit of detection (LOD) and limit of quantification (LOQ) of the method was based on the analysis of 20 consecutive matrix-blank samples that were prepared independently based on Wenzl et al. (2016). The LOD was calculated as 3.5 times the standard deviation of the signals of the blanks divided by the slope of the calibration curve and the LOQ was calculated as 3.3 times the LOD. This resulted in LOQ values of 0.015 µg Ag/L and 0.16 µg Ti/L. Measurements below the calculated LOQ are reported as <LOQ.

2.5. Calculations and expression of results

Concentration (c) of Ag or Ti expressed in µg/g sample that leached after determined contact time (1, 4, 8, 24 h) was calculated with Eq. (1):

$$c = (V \times df \times C) / W \quad (1)$$

where V (mL) is the extraction volume of acid sweat, df is the dilution factor prior to ICP-MS measurement, C (µg/L) is the concentration of Ag or Ti measured in the diluted leachate solutions and W (g) is the weight of the piece of face mask (or face mask layer) sample (6 cm × 6 cm). To express release of Ag or Ti in µg/mask the average weight of the respective face mask was considered. For masks composed of different layers the average weight of each layer was considered and the total release of Ag or Ti per mask was calculated by the sum of the release of each layer.

2.6. Statistical analysis

Means and standard deviations were calculated for duplicate samples. Single-factor analysis of variance (ANOVA) per mask was conducted to investigate if the leaching time (1, 4, 8, 24 h) had an effect on the amount of Ag and Ti released in the artificial sweat. The level of significance was set at P value <0.05. Prior to conducting the ANOVA analysis, data was assessed for its normal distribution using the Shapiro-Wilk's test. All statistical analyses were performed using statistical program R- RStudio 2022.02.0.

3. Results and discussion

3.1. Selection of leaching solution and size of the piece of face mask

In the absence of a generally accepted standard protocol that simulates the conditions of the liquid in saturated breathed air, our leaching experiments were aligned with previous studies that investigated metal leaching from textiles in close contact with the skin using artificial human sweat solutions (Herrero et al., 2019; Kulthong et al., 2010; von Goetz et al., 2013; Wagener et al., 2016). These leaching solutions provide some type of chemical stress that can stimulate the release of metals from the textiles due to acidic or basic pH and high salt concentration. Although there is no unique protocol to prepare artificial human sweat solutions, a number of published scientific work that evaluated the release of metals from textiles, followed the protocol described in the ISO procedure 105-E04 for 'colour fastness to perspiration' (ISO, 2013). In this ISO protocol the pH of the artificial sweat solution can be adjusted to pH 5.5 or 8.0 using NaOH. To test the migration of Ti and Ag from the face masks in this study, the artificial sweat was adjusted to pH 5.5, since it was considered that the pH of human sweat is slightly acidic with reported median pH 5.3 (Harvey et al., 2010). This can also be considered a worst-case pH compared to exhaled breath condensate (pH ranging 6.2–7.8) (Aldakheel et al., 2016).

Although no formal confirmation is available, the size of the pieces of face mask applied in the leaching experiment might influence the leaching of Ag and Ti from face mask to artificial sweat. Smaller sizes might expose a relatively larger fraction of sectioned fibres than larger pieces, such that a higher fraction of particles from the fibre interior are at the surface and susceptible to particle release. There is no standard methodology to investigate the release of metals and nanoparticles from textiles in leaching experiments and different solid-to-liquid ratios have been used. This also makes it difficult to compare results between different studies since the conditions for leaching varies. For example, Mackevica et al. (2017) conducted leaching experiments using pieces of textile of 20 cm × 20 cm that were immersed in 200 mL of solution (ratio 2 area:volume), Suwanroek et al. (2022) used pieces of textiles of 4 cm × 4 cm and 10 mL solution (ratio 1.6 area:volume) and Pollard et al. (2021) used pieces of 2 cm² and 10 mL solution (ratio 0.2 area:volume). In this study, the size of the piece of mask for the leaching experiment was selected such that it is representative for the entire mask. If smaller pieces need to be tested, the size effect can be minimized adjusting the volume of solution to assure the same solid-to-liquid ratio, for example 1.8 area:volume, as applied in this study.

3.2. Release of Ag in leaching experiments

Face masks AgMask-05 and AgMask-11 contained no Ag (Mast et al., 2023) and were included in the experiment as negative controls. No Ag was detected in the leachates of these masks after the different equilibration times i.e. 1, 4, 8, 24 h (data not shown). Additionally, no Ag was detected in the control blank samples containing no face mask.

Silver was released into artificial acid sweat in concentrations above the LOQ in the following face masks: AgMask-08, AgMask-15, AgMask-18 and AgMask-20 (Table 2). In general, the highest amounts of Ag that leached out into acid sweat were observed in the external or outermost layer and internal or innermost layer of AgMask-08 with over 20 µg Ag/g sample. The central or middle layer of AgMask-08 which consisted of 4 layers of non-woven fabric, also released Ag, although at much lower concentrations <2 µg Ag/g sample. As reported previously by Mast et al. (2023) the external and internal layers of AgMask-08 contained much higher total Ag content (82 mg Ag/g) compared with the central layer (0.08 mg Ag/g). It appears that the difference in the degree of leaching in the external and internal layer compared to the central layer can be related to their initial total Ag content. Electron microscopy analysis showed that the woven fibres of the external and internal layers were

Table 2
Release of Ag into artificial acid sweat for face masks: AgMask-08, AgMask-15, AgMask-18 and AgMask-20.

Face mask	Layer	Contact time	Amount of Ag leached	Ag leached per mask	Ag leached
		(h)	($\mu\text{g Ag/g sample}$) ^a	($\mu\text{g Ag/mask}$) ^b	(% of total Ag content)
AgMask08	External	1	22.1 \pm 1.1	61 \pm 6	0.03
		Central	1.3 \pm 0.5		
		Internal	23.1 \pm 4.1		
	External	4	26.6 \pm 2.3	66 \pm 3	0.03
		Central	1.2 \pm 0.3		
		Internal	23.0 \pm 1.3		
	External	8	23.8 \pm 0.8	65 \pm 3	0.03
		Central	1.63 \pm 0.02		
		Internal	24.4 \pm 2.5		
External	24	21.3 \pm 0.5	59 \pm 2	0.03	
	Central	1.8 \pm 0.5			
	Internal	21.8 \pm 0.8			
AgMask15	All	1	0.94 \pm 0.02	9.3 \pm 0.2	6
	All	4	0.88 \pm 0.02	8.8 \pm 0.2	5
	All	8	0.97 \pm 0.16	9.6 \pm 1.6	6
	All	24	0.87 \pm 0.10	8.6 \pm 1.0	5
AgMask18	External	1	8.8 \pm 0.3	51 \pm 3	29
		Internal	8.2 \pm 0.9		
	External	8	12.3 \pm 5.8	76 \pm 23	43
		Internal	13.0 \pm 5.0		
AgMask20	External	1	<LOQ	0.09 \pm 0.05	1
		Central	4.9 \pm 2.8		
		Internal	<LOQ		
	External	8	<LOQ	0.30 \pm 0.06	5
		Central	16 \pm 3.2		
		Internal	<LOQ		

^a Average of duplicates \pm standard deviation.

^b For masks AgMask-08 and AgMask-18 that contain layers Ag leached per mask is calculated as the sum of Ag released of each layer. The propagated error is calculated from the addition of individual standard deviation as follows: $\sigma_{Ag_{mask}} = \sqrt{[(\sigma_{Ag_{external}})^2 + (\sigma_{Ag_{central}})^2 + (\sigma_{Ag_{internal}})^2]}$; where, $\sigma_{Ag_{external}}$, $\sigma_{Ag_{central}}$ and $\sigma_{Ag_{internal}}$ are the standard deviations for Ag leached in the external, central and internal layers. For AgMask-15 Ag leached per mask is the average of duplicates \pm the standard deviation. For AgMask-20 Ag leached per mask corresponds to the average Ag leached in the central layer \pm the standard deviation.

coated with Ag⁰ nanoparticles and that the coating was damaged or incomplete in many areas (Mast et al., 2023). The presence of Ag in the central layer can be explained by the observed damage of the coating, resulting in detached Ag⁰ nanoparticles in the central layer.

Face mask AgMask-15 consisted of an external and internal layer of polyamide containing about 80 μg of Ag each. Since both layers were identical in material composition and Ag content the layers were not separated for the leaching experiments. As shown in Table 2, the release of Ag was $<1 \mu\text{g Ag/g sample}$ and the amount of Ag that released to the acid sweat reached a maximum after 1 h remaining relatively constant in the following leaching times. Mast et al. (2023) showed that in AgMask-15, Ag was present as nanoparticles which were in large part encapsulated in the polymer fibres arguing that most of this nanoparticulate Ag would be unavailable for release. The lower release of Ag per g of material in AgMask-15 supports this observation.

Face mask AgMask-18 was made of two identical layers containing polyester, polyamide and elastane. The leaching experiment was conducted on separate layers (external, internal) since the Ag content differed in both layers (66 μg Ag external layer vs. 110 μg Ag internal layer) (Mast et al., 2022). As shown in Table 2, the release of Ag increased from 8 $\mu\text{g Ag/g}$ up to 13 $\mu\text{g Ag/g}$ when contact times increased from 1 h or 8 h. Face mask AgMask-20 was composed of three different layers, the external and internal layer were made of non-woven fabric and the central layer of nanofibre membrane. The central layer

contained the highest amount of Ag (5.4 μg) while the external and internal layer contained 0.5 μg Ag and 1.2 μg Ag, respectively (Mast et al., 2022). As shown in Table 2, Ag released in detectable concentrations only from the central layer and the amount of Ag released after 8 h contact time was about three times higher compared to 1 h contact time.

Across all face masks the average amount of Ag released per mask followed the decreasing order: AgMask-08 \sim AgMask-18 $>$ AgMask-15 \gg AgMask-20 (Table 2). Face mask AgMask-08 and AgMask-18 had similar levels of total Ag release per mask, (63 $\mu\text{g Ag/mask}$ average of 4 leaching times for AgMask-08 and 64 $\mu\text{g Ag/mask}$ average of 2 leaching times for AgMask-18), despite AgMask-08 having more than thousand times higher total Ag content. When the release is expressed as percent of total Ag content, AgMask-08 yielded the lowest percent of released Ag (0.03 %) compared to AgMask-18 (36 %). In addition, despite AgMask-15 and AgMask-18 having more or less similar total Ag content (165 vs 176 $\mu\text{g Ag}$), the percentage of Ag released was 6.5 times higher in AgMask-18 than AgMask-15. The differences can be related to the form of Ag biocide present in the fabric and also on the functionalization technology. For example, Wagener et al. (2016) reported between 8 and 75 % of total Ag content released into artificial sweat in textiles where Ag was added as a surface coating, whereas either no release or $<8 \%$ of total Ag content was released in textiles where Ag was embedded as a nanocomposite in the fabric. Furthermore the authors concluded that the release of Ag predominantly occurred as dissolved Ag (Wagener et al., 2016). In the present study, AgMask-08 contained Ag⁺ ions and also Ag nanoparticles in the outside and inside of the fibres added as a coating, for AgMask-18, Ag is present as Ag⁺ ions, and AgMask-15, Ag is added as Ag nanoparticles encapsulated in the polymer fibres (Mast et al., 2023).

Comparing the release of Ag into the sweat solution under the different contact times, no significant differences (P value >0.05) were observed between the amount of Ag released from face mask AgMask-08 and AgMask-15. This suggests that an extended exposure of the fabrics to sweat through wearing does not necessarily result in a higher release of Ag. Similar Ag leaching kinetic behaviour has been reported previously by Quadros et al. (2013) and von Goetz et al. (2013) for Ag-containing textiles in contact with artificial sweat. These leaching kinetics can be used to refine the safety assessment of reusable face masks. For example Mast et al. (2023) argued that for reusable face masks the daily exposure to Ag can be reduced as the amount of Ag released assumed to be linear over time, hence impacting the safety assessment of face masks. In contrast, our results showed that release of Ag is not gradual and in general the maximum amount of released Ag was reached after 1 h of contact time with the leaching solution.

Finally, in four face masks AgMask-03, AgMask-12, AgMask-13, AgMask-14 no Ag was detected in the artificial sweat for any of the contact times. AgMask-03 contained three distinctive layers external, central and internal and Ag was only found in the external layer (Mast et al., 2022). In situ electron microscopy analysis showed that at least a fraction of the total Ag was present as Ag nanoparticles which were observed at the surface or close to the cotton fibres (Mast et al., 2022). In face mask AgMask-13, Ag was detected in the external and internal layers while in AgMask-14, Ag was detected in the central and internal layer. No Ag particles were observed by electron microscopy in these face masks, Ag was mainly present as Ag⁺ ions (Mast et al., 2022). In these face masks (AgMask-03, AgMask-12, AgMask-13, AgMask-14) it can be speculated that Ag was not detected in the artificial sweat because either the amount of Ag present in the mask was too low to release Ag above the limit of detection, the coating of Ag was unevenly distributed in the face mask or for the specific case of AgMask-03, Ag remained strongly bound to polycationic polymers (Silvadur™ technology) which were incorporated in the fibres and thus not easily leachable.

3.3. Release of Ti in leaching experiments

All investigated face masks contained Ti as TiO₂ particles with contents ranging from 11 to 152,345 µg TiO₂/mask (Table 1). From the ten face masks investigated, only mask AgMask-18 released Ti into artificial sweat in measurable amounts (Table 3). The total percent release of Ti per mask was 0.35 % (average of two leaching times). In the previous work, Mast et al., 2021 demonstrated the presence of TiO₂ particles in polyester and polyamide fibres with most of the particles located inside the fibres, although also some particles can be present at the surface of the fibre (Mast et al., 2021). Presumably in this particular mask, TiO₂ particles at the surface were the ones that released during the leaching experiment since, supporting on the considerations of Franz et al. (2020) larger particles firmly incorporated into the fibre do not leach out.

In general the results from this work agree with other published studies that investigated the migration of TiO₂ particles from textiles in artificial solutions. For example, von Goetz et al. (2013) reported release of particulate TiO₂ in artificial sweat from a textile composed of polyester and wool and no dissolved Ti was detected in the leachate solutions after ultrafiltration. It was speculated that the migration of TiO₂ particles in this particulate fabric was because they were added as a coating and hence not embedded in the fabric (von Goetz et al., 2013). In the work by (Rovira et al., 2017) Ti released in only one of the samples in detectable concentrations and the percent release was low (7 % of total Ti content).

3.4. Refinement of the preliminary risk assessment with leaching data

A conventional risk assessment of the potential risks associated with the inhalation of Ag-based biocides and TiO₂ particles from normal wearing of face masks is to date not possible due to the lack of exposure data. Hence, in order to evaluate whether face masks are safe by design, an indirect approach for risk assessment was proposed by comparing the total amount per mask of Ag or TiO₂ to their respective acceptable amount of releasable (AEL_{mask}) Ag or TiO₂ per mask (Mast et al., 2023; Verleysen et al., 2022). The AEL_{mask} in this context is the maximum amount of Ag or TiO₂ that can be released and inhaled during mask usage without generating safety concerns (i.e. intrinsically safe masks). For details on how the different AEL_{mask} for Ag and TiO₂ were determined the reader is referred to Mast et al., 2023 and Verleysen et al., 2022. Briefly, for calculation of AEL_{mask} the following general equation was used:

$$AEL_{\text{mask}} = \frac{\text{critical dose}}{\text{uncertainty factor}} \times \text{inhaled air volume} \times \text{Duration.}$$

The critical dose and estimated uncertainty factor were different for Ag and TiO₂. As indicated in Mast et al. (2023) the critical dose used for Ag is the occupational exposure limit (OEL) of 10 µg/m³ for Ag in generic form (i.e. metal dust, fume, soluble compounds) and 0.9 µg/m³

Table 3
Amount of Ti released into artificial acid sweat for face mask AgMask-18.

Face mask	Layer	Contact time	Amount of Ti leached	Ti leached per mask	Ti leached
		(h)	(µg Ti/g sample) ^a	(µg Ti/mask) ^b	(% of total Ti content)
AgMask18	External	1	5.5 ± 1.6	34 ± 7	0.3
		8	5.7 ± 1.8		
	Internal	1	8.4 ± 6.0	47 ± 24	0.4
		8	7.1 ± 5.1		

^a Average of duplicates ± standard deviation.

^b For mask AgMask-18 that contain layers Ti leached per mask is calculated as the sum of Ti released of each layer. The propagated error is calculated from the addition of individual standard deviation as follows: $\sigma_{Ti_{\text{mask}}} = \sqrt{[(\sigma_{Ti_{\text{external}}})^2 + (\sigma_{Ti_{\text{internal}}})^2]}$; where, $\sigma_{Ti_{\text{external}}}$, and $\sigma_{Ti_{\text{internal}}}$ are the standard deviations for Ti leached in the external and internal layers.

for Ag nanoparticles, which were defined by the National Institute for Occupational Safety and Health (NIOSH). Since the OEL limit values were intended for the professional population and the masks of the study are sold for the general population an uncertainty factor of 2 was used to consider higher variability among the general population (Mast et al., 2023). The inhaled volume was set to 1.25 m³/h and the duration refers to the number of hours of mask usage. An intensive usage scenario of 2 masks per day each worn for 4 h was selected. With this consideration, two limit values were calculated for Ag, an AEL_{mask} of 25 µg for Ag as metal dust, fume, and soluble compounds and an AEL_{mask} of 2.25 µg for Ag in nanoparticulate form (Mast et al., 2023). For TiO₂ an AEL_{mask} of 3.6 µg was estimated using threshold based risk analysis for subchronic exposure and an intensive mask usage scenario (Verleysen et al., 2022). The critical dose used was the human equivalent concentration of the no observed adverse effect concentration (NOAEC_{HEC}) based on the repeated dose inhalation study conducted in rats by Bermudez et al. (2004). The calculated NOAEC_{HEC} is 0.065 mg TiO₂/m³. An uncertainty factor of 90 was estimated which considers inter-species variability (factor 3), intra-human variability (factor 10) and adjustment for the inadequacy of the database (factor 3) (Verleysen et al., 2022). Using the indirect approach for risk assessment, masks for which total amounts of Ag or TiO₂ are below the AEL_{mask} can be considered as intrinsically safe, while masks with total amounts of Ag and TiO₂ above the AEL_{mask} required a further risk evaluation. This is a conservative approach which can overestimate the risks but considering the lack of direct exposure and/or release data, it was also the best possible way to estimate potential risks.

Although the conditions during leaching experiments do not resemble those during the normal wearing of face masks, it was considered that the experimental conditions in such experiments are more stringent than those occurring during normal use of face masks. For example, face mask samples are completely immersed in a solution of acidic pH and high salt concentration (artificial acid sweat) and they are subjected to physical stress since the tubes containing the samples were shaken at a moderate speed in the overhead shaker. Hence, leaching experiments can be applied as an alternative and relatively cheap method to evaluate the quality of face masks, providing a more refined assessment when the face masks are not safe-by-design according to the preliminary risk assessment applied by Mast et al., 2023 and Verleysen et al., 2022.

As a proof of concept, the results of the leaching experiments were used to refine the preliminary risk assessment comparing the leachable Ag or Ti per mask with the threshold values (AEL_{mask}). Table 4 shows that for AgMask-08 and AgMask-18 the leachable Ag per mask is higher than the AEL_{mask}, indicating that these face masks would need a further refined safety assessment. For AgMask-15 the leachable Ag is below the AEL_{mask} (using the threshold limit for generic Ag) but when the ratio is calculated using the threshold for Ag nanoparticles it shows that AgMask-15 would need further assessment. For masks AgMask-03 and AgMask-14, no ratio could be calculated since in these face masks Ag was not detected in the acid sweat leachates. Based on the leaching test approach these masks can be considered safe, however, as they failed to pass the safe-by-design calculations based on total Ag content further evaluations should be considered. The risk evaluation could be also refined for TiO₂ using the leaching data (Table 4). Titanium was detected only in the leachate of mask AgMask-18 and the amount of Ti released after 8 h was 47 µg Ti/mask (78 µg TiO₂/mask). This amount is 22 times higher than the threshold AEL_{mask} value (3.6 µg). Hence this mask would require further safety assessment.

The evaluation of masks that are safe-by-design based on leaching data is less conservative than the approach that uses total element content in the mask. This “proxy approach”, which is also a conservative one, allowed to bypass the technical challenges encountered by the lack of methodology to determine and quantify release of Ag-biocides and TiO₂ particles from face masks in conditions that mimic real wearing. With these considerations, face masks AgMask-08, AgMask-15 and

Table 4

Exceedance ratios for Ag and TiO₂ calculated using the total silver and TiO₂ content per mask or the leachable Ag and leachable TiO₂ per mask divided by their respective limit value (25 µg Ag in generic form, 2.25 µg Ag nanoparticles or 3.6 µg TiO₂).

Face mask	Times total Ag exceeds AEL _{mask} ^a	Times leachable Ag exceeds AEL _{mask} ^b	Times total TiO ₂ exceeds AEL _{mask} ^c	Times leachable TiO ₂ exceeds AEL _{mask} ^d
AgMask-03	1.5/16	N.A.	8542	N.A.
AgMask-05	N.A.	N.A.	220	N.A.
AgMask-08	9402/104464	2.6/29	3416	N.A.
AgMask-11	N.A.	N.A.	3	N.A.
AgMask-12	0.3/(–)	N.A.	2271	N.A.
AgMask-13	0.5/(–)	N.A.	3388	N.A.
AgMask-14	3.5/(–)	N.A.	8	N.A.
AgMask-15	6.6/73	0.4/4.3	42318	N.A.
AgMask-18	7.0/(–)	3/(–)	5318	22
AgMask-20	0.3/(–)	0.01/(–)	638	N.A.

N.A.: Denotes that ratios were not calculated as Ag or Ti were not detected in the leachates or in the face mask.

(–) denotes that ratio was not calculated using Ag nanoparticle AEL threshold since Ag is only present as Ag⁺ ions in these face mask (Mast et al., 2023).

^a Ratio of total Ag content per mask by limit value. The value before the slash is calculated using the generic threshold limit for Ag and the value after the slash is calculated using the threshold limit for Ag nanoparticles.

^b Ratio of leachable Ag per mask by limit value. The value before the slash is calculated using the generic threshold limit for Ag and the value after the slash is calculated using the threshold limit for Ag nanoparticles.

^c Ratio of total TiO₂ content per mask by limit value.

^d Ratio of leachable TiO₂ per mask by limit value.

AgMask-18 failed to pass this proxy test. It is important to note that in the proposed approach the obtained leachate samples were not subjected to a strong acid digestion step as we intended for a simple method that would allow fast screening of large number of samples. Nevertheless it is recommended to consider digestion of the leachates when nanoparticles are present in the textiles and the measured release concentration of Ag or TiO₂ per mask are close or lower than the selected AEL threshold values. In such a scenario a more accurate quantification of total release is needed to avoid the situation of having a mask not failing the proxy test when it should.

4. Conclusions

In this work a simple method was used to estimate the release of Ag and Ti from face masks. The method used a type of chemical stress (i.e. acidic pH of the artificial sweat solution) and physical stress (i.e. overhead shaking) such that the applied leaching conditions can be considered to be more stringent than those occurring during normal face mask wearing. As proof-of-concept, leaching experiments were shown to be useful as an additional tool to evaluate the quality of face masks, and as a higher tier method to refine the risk assessment when the face masks are not safe-by-design. Following the risk assessment approach using leaching data, three face masks out of the ten investigated would require further risk analysis for Ag since the amount of leachable Ag surpassed the selected threshold values for Ag in generic form and/or for Ag in nanoparticulate form. The common characteristic in these face masks was their high total Ag content (165, 176, 235044 µg Ag/mask). In the present work, leaching of Ag was higher in layers of face masks where Ag

was added as coating (i.e. external and internal layers of AgMask-08) compared to those where Ag was fully integrated as a nanoparticle in the fibre (i.e. AgMask-15) when expressed in absolute values (i.e. µg Ag/mask). Hence the extent of release depends on the functionalization technology. The risk assessment of TiO₂ showed that only one mask would require further analysis. Despite that TiO₂ was present in large amounts and in all of the face masks investigated, the release of Ti was only detected in one face mask. The plausible explanation for the limited release of Ti can be related to the localization of TiO₂ particles in the fibres of the textile. In this sense our work aligns well with other published studies.

While we recognise that the application of nanotechnology has led to advances of the textile industry through the production of fabrics with desired or improved functional qualities, there is increasing awareness from the consumers' side regarding the potential risks of such applications. In that sense it is important that regulatory standards are in place to protect the consumers. To this end, methods (i.e. leaching experiments) that facilitate the evaluation of the potential release of selected chemicals from face masks should be further developed, standardized and validated. In this perspective, material-specific reference materials required for method optimization and evaluation are missing and hence need to be developed.

CRedit authorship contribution statement

Daniela Montalvo: conceptualization, methodology, data analysis, investigation, supervision, writing - original draft; **Gabriel M. Mercier:** methodology, investigation, writing – review and editing; **Jan Mast:** resources, supervision, funding acquisition, writing – review and editing; **Karlien Cheyns:** conceptualization, methodology, supervision, resources, writing – review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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