



HAL
open science

Towards a surface metric to measure the dustiness of nanomaterial powders

Claire Dazon, Sébastien Bau, Raphaël Payet, Vanessa Fierro, Olivier Witschger

► **To cite this version:**

Claire Dazon, Sébastien Bau, Raphaël Payet, Vanessa Fierro, Olivier Witschger. Towards a surface metric to measure the dustiness of nanomaterial powders. *Environmental Science: Processes & Impacts*, 2023, 25 (3), pp.670-679. 10.1039/D2EM00514J . hal-04275426

HAL Id: hal-04275426

<https://hal.univ-lorraine.fr/hal-04275426>

Submitted on 8 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Towards a surface metric to measure the dustiness of nanomaterial powders

2
3 *Claire Dazon^{a*}, Sébastien Bau^b, Raphaël Payet^b, Vanessa Fierro^c and Olivier Witschger^b*

4
5 ^a Ecole Supérieure de Physique et de Chimie Industrielles de la ville de Paris, Paris

6 ^b Aerosol Metrology Laboratory, INRS, Vandoeuvre, France

7 ^c Institut Jean Lamour - UMR CNRS 7198, Epinal, France

8 *E-mail corresponding author: dazonclaire@gmail.com

9 10 **Abstract**

11
12 The relevance of dustiness methods is increasingly recognized in the preliminary exposure
13 evaluation of workers handling nanomaterials in powder form, and should also be transposed
14 to the assessment of environmental risk in the future. So far, the methods recommended in the
15 current European standards mainly indicate to determine a mass-based dustiness index
16 [mg.kg⁻¹], whereas the surface area is regularly put forward as a more appropriate determinant
17 to assess the pulmonary toxicity of nanoparticles. In this study, we describe an operational
18 methodology leading us to propose a surface metric to determine the dustiness index [m².kg⁻¹]
19 of nanoparticulate matter. To this end, we demonstrate the equivalence between the external
20 specific surface area of a nanopowder and that of its aerosol with five nanomaterials produced
21 and used on an industrial scale, and covering a range of external specific surface areas from
22 35 to 230 m².g⁻¹. Compared to the conventional mass-based dustiness index, the surface-based
23 dustiness index is 1) more discriminating, allowing to cover an additional order of magnitude,
24 and 2) has an impact on the powder ranking with potential consequences on the preventive
25 measures to be implemented. Finally, our proposal has the potential to be included in future
26 revisions of European standards for workplace exposure and dustiness measurement, provided
27 that further experimental results on surface-based dustiness indices comfort these preliminary
28 data.

29
30 **Keywords:** Nanomaterials, dustiness, powders, surface area, workplace exposure.

35

36 **1.Introduction**

37 Nanomaterials in powder form are increasingly used in industry and laboratories, and this
38 trend should continue in the coming years. Their promising properties allow them to be used
39 in many fields of application, such as food, buildings, cosmetics, textiles, pharmaceuticals to
40 name but a few ^[1-4]. Amongst the many evidences of this wide diffusion of powdered
41 nanomaterials, the latest R-nano 2020 report on the mandatory declaration of production,
42 importation or distribution of nanomaterials in France indicates that nearly 500 000 tons of
43 nanomaterials are declared ^[5]. Although the reporting of the form of the substances is not
44 detailed enough, most of the chemicals appear to be powders ^[6].

45 In the workplace, inhalation exposures to airborne particles when handling (nano)powders
46 during bagging, transferring and/or cleaning are possible throughout the product life cycle ^[7-9],
47 but exposure data remain very scarce. This may be partly due to the lack of harmonized
48 strategies for measuring exposures; these remain complex to implement in workplaces
49 although proposals have been made in this respect ^[10-13]. Most recently, Froggett et al. ^[14]
50 have highlighted the need to develop methods capable of measuring the release potential of
51 (nano)particles in different work situations. A formidable response can be proposed today to
52 this difficult task of accurately measuring inhalation exposures to nanomaterials, and it relies
53 on the deployment of dustiness methods in companies and laboratories where nanomaterial
54 powders are encountered (produced, processed, used). These methods are increasingly
55 recognized as relevant approaches to initially estimate workplace exposures of employees
56 handling powdered (nano)materials as a preamble to more robust documentation and accurate
57 exposure measurements ^[15-17]. The dustiness of a powder is defined as its propensity to
58 generate airborne particles during handling or after mechanical stimuli (drop, fluidization,
59 shaking) ^[18]. This definition can be extended to any particulate material, including pellets and
60 granules. Dustiness data can be used to classify powders according to their dustiness indices,
61 or incorporated in exposure models to estimate the amount of (nano)particles potentially
62 released into the workplace atmosphere. Dustiness is also an input descriptor of the material
63 for exposure control by banding approaches ^[19-22], and in safe-by-design approaches for the
64 responsible development of products containing nanoparticles. Moreover, dustiness could be a
65 mandatory data item in the future REACH documentation in the context of chemicals
66 regulation ^[23]. In order to assess the relevance and reliability of the measurement of the
67 dustiness indices of a powder, several institutions such as OECD or ECHA have initiated
68 projects for preventive measures against chemical risks. Last, but not least, environmental

69 safety should also be assessed by dustiness measurements, in order to prevent or predict the
70 potential for dust explosion in industrial atmospheres as highlighted by Klippel et al. [24]. For
71 instance, knowledge of dustiness should be used to optimize the determination of explosive
72 areas, to manage ventilation systems and/or to set suppressing systems. While environmental
73 safety is currently less evaluated by research results than health risks, the growing concern for
74 environmental safety in workplaces should reverse this trend in favor of more research on this
75 topic. Dustiness is determined through dedicated methods, which are described in European
76 standards, five of which have recently been revised, and adapted to nanoparticulate matter,
77 encompassing all types of particulate matter [25-29]. The dustiness method to be used is chosen
78 according to 1) the type of particles considered (nanoparticles, non-nanoparticles, pellets,
79 granules, etc...) and 2) the workplace exposure scenario to mimic. Four methods are available,
80 namely the Rotating Drum (RD), the Continuous Drop (CD), the Small Rotating Drum (SRD),
81 a reduced version of the RD, and the Vortex Shaker (VS).

82 The dustiness of a powder is determined through a mass-based index, which may be
83 accompanied by a number-based index, in line with at least one of the three conventional
84 health-related fractions (inhalable, thoracic and respirable) [30]. Amongst the sole laboratory
85 measurements of dustiness, a possibility to correlate the obtained indices with measured
86 workplace exposures or exposure modelling has recently emerged with the example of
87 nanoclays particles and fertilizers handling in different workplaces [31-34]. These works that
88 correlate dustiness data with workplace exposures support the importance of measuring
89 dustiness in laboratory using an appropriate method described in the standards, and using it as
90 a proxy for estimating inhalation exposures, as a preamble to a thorough measurement
91 campaign in the workplace. Though mass- and number-based metrics are commonly used for
92 dustiness measurements, surface area is increasingly recognized as a relevant parameter for
93 assessing the pulmonary toxicity of insoluble or poorly soluble nanomaterials [35-41]. Given the
94 importance of investigating different relevant parameters to assess the toxicological effect of
95 nanoparticles on human health, surface area could be incorporated into European dustiness
96 standards to complete the existing metrics. Multi-metric documentation of exposure is a
97 common trend to follow when seeking to reduce occupational risks associated with airborne
98 particles^[42].

99 Such a consideration implies an accurate measurement of the surface area of airborne
100 nanoparticles resulting from the aerosolization of nanomaterial powders. Gas adsorption can
101 be considered as a reproducible reference method for measuring the surface area of solid
102 particles^[43]. The surface area per gram of material is commonly determined applying the

103 BET model ^[44] to the nitrogen adsorption data for non-porous, macroporous or mesoporous
104 powders, we referred then as the external specific surface area (A_{Ex} , $\text{m}^2\cdot\text{g}^{-1}$), whereas the t-
105 plot model is more adequate for microporous materials. Adsorption isotherm models were
106 defined by the International Union of Pure and Applied Chemistry (IUPAC), as well as the
107 data processing to determine the specific surface area ^[45]. A_{Ex} is an integral method,
108 accounting for all particles present in the sample, from which an equivalent constituent
109 particle diameter can be derived. In the paper from Bau et al. ^[46], the issue of particle
110 polydispersion is investigated both theoretically and experimentally on a set of 8 powder
111 materials.

112 Based on this, it would be interesting to integrate an additional dustiness index accounting for
113 the external surface area. However, this relies on the measurement of the A_{Ex} of airborne
114 particles released during a dustiness test. Performing gas adsorption on a powder sample to
115 determine its A_{Ex} is relatively straightforward. However, it remains particularly tricky to
116 apply this technique to aerosols, since particles are in motion and dispersed in a surrounding
117 gas. Devices based on diffusion charging give access to the geometric, active or lung-
118 deposited surface area ^[47-48] but their performance has not been studied for airborne particles
119 emitted by powders and they are limited to a particle size range of 10 nm to a few μm , which
120 is not sufficient to measure those expected for a powder-based aerosol (between 10 nm and
121 over 10 μm). Lebouf et al. ^[49] proposed a methodology to determine the A_{Ex} of particles
122 collected on filters for different aerosols of nano TiO_2 , between 55 and 160 $\text{m}^2\cdot\text{g}^{-1}$, and nano
123 SiO_2 ($57 \text{ m}^2\cdot\text{g}^{-1}$) generated in an inhalation chamber for toxicology experiments. The authors
124 proposed an approach based on the difference in surface area measurement between a
125 sampled and blank collecting support. Bau et al. ^[50] proposed another strategy based on TEM
126 observations to determine the A_{Ex} , of SiO_2 , ZrO_2 , Al_2O_3 , Fe_2O_3 and Fe_3O_4 nanomaterial
127 powders, between 20 and 200 $\text{m}^2\cdot\text{g}^{-1}$, where the aerosols were generated with a vortex shaker
128 dustiness method. A close agreement between the TEM-based method and the gas adsorption
129 measurement for determining the A_{Ex} was observed. However, the particles analyzed in the
130 TEM-based method were aerosolized and the adsorption measurements were performed
131 directly on the powders, not on the collected particles, which assumes equivalence between
132 the surface areas of powders and their aerosols. The authors assumed this equivalence but it
133 has not been experimentally demonstrated, which could invalidate their conclusions. A similar
134 approach with automatic particle analysis was also used by Bourrous et al. ^[51].

135 In this context, we describe in this paper an operational methodology leading us to propose a
136 surface-based dustiness index [$\text{m}^2\cdot\text{kg}^{-1}$] that could be used for dustiness test measurements.

137 This index involves the mass-based dustiness index of airborne particles determined using a
138 reference dustiness method, combined with their external specific surface area based on
139 equivalence with that of powders. This equivalence is demonstrated experimentally through
140 powder-borne aerosols generated by an SRD dustiness method coupled with a cascade
141 impactor to collect the released particles. Gas adsorption was performed to measure both the
142 powders and powder-borne external specific surface areas. All powders are identified as
143 nanomaterials and are among the most common nanoparticles encountered in workplaces.
144 Then, the proposed surface-based dustiness index was implemented on the available literature
145 data from the CEN Dustinano pre-normative research programme (SA/CEN/ENTR/461/2012-
146 06, Mandate M/461) and compared to the conventional mass based-dustiness index.
147
148

149 **2. Concept of the surface-based dustiness index**

150 The concept of surface-based dustiness index relies on combining a mass-based dustiness
151 index determined with any of the dustiness methods and the external specific surface area of
152 airborne particles generated during the dustiness test (equations 1 and 2).

153

$$DI_S(\text{m}^2/\text{kg}) = \frac{\Delta m \cdot A_{Ex}(\text{collected particles})}{M_0} \quad (1)$$

$$DI_S(\text{m}^2/\text{kg}) = DI_M \times A_{Ex}(\text{collected particles}) \quad (2)$$

154

155 Δm is the airborne particle mass (in g) released and collected during the dustiness test and
156 determined by gravimetric analysis. M_0 is the powder sample mass (in kg) introduced in the
157 system associated with the dustiness method. $A_{Ex}(\text{collected particles})$ is the external specific surface
158 area ($\text{m}^2 \cdot \text{g}^{-1}$) of the airborne particle sample measured with gas adsorption. However, the
159 measurement of $A_{Ex}(\text{collected particles})$ is relatively difficult as mentioned before. In most cases,
160 the collection media used in dustiness tests are not designed to be introduced into
161 conventional gas adsorption cells. Another issue is the small amount of collected airborne
162 particles on the media. On one hand, this quantity can be as low as $\approx 10 \mu\text{g}$ for the less dusty
163 powders, resulting in approximate results due to measurement uncertainties. On the other
164 hand, because reliable gas adsorption measurements require a minimum surface of 10 m^2 to
165 be analyzed, a quantity of 100 mg of particles with an A_{Ex} of $100 \text{ m}^2 \cdot \text{g}^{-1}$ would be necessary.
166 The amount of particles produced in dustiness test benches is therefore not in line with the
167 one required for the gas adsorption analysis. Consequently, to simplify our proposal, it has
168 become crucial to demonstrate the equivalence between the powder external specific surface
169 area and that of their corresponding aerosols in such a way that $A_{Ex}(\text{collected particles})$ in equation 1
170 can be substituted by $A_{Ex}(\text{powder})$, this latter being much easier to measure as aforementioned.

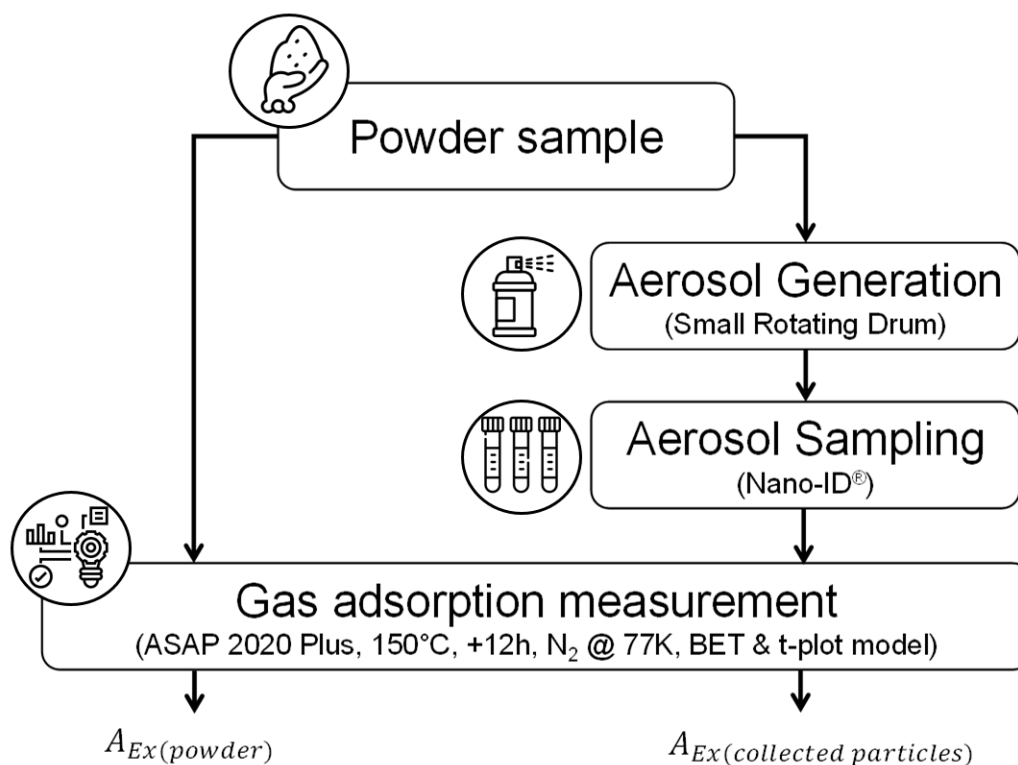
171

172 **3. Experimental Section**

173 **3.1. Experimental Methodology**

174 A flowchart describing the experimental approach carried out for the demonstration of the
175 equivalence between $A_{Ex}(\text{powder})$ and $A_{Ex}(\text{collected particles})$ is represented on **Figure 1**.

176



177
178
179

Figure 1: Flowchart of the experimental approach carried out to demonstrate the equivalence between external specific surface area of powders and their corresponding aerosols.

180 A part of a powder sample is directly analyzed with the gas adsorption technique to determine
181 its $A_{Ex(\text{powder})}$, whereas another part of the sample is used for aerosol generation with the Small
182 Rotating Drum (SRD) dustiness method ^[28] combined with a cascade impactor (Nano-ID[®]) to
183 collect particles for subsequent gas adsorption analysis to determine the $A_{Ex(\text{collected particles})}$.
184 The next sections detail each part of the methodology.

185 3.2.Powders

186 For this study, five industrial powders, representative of the most encountered materials in
187 workplaces, were selected. These powders were studied and characterized among a set of ten
188 materials in the European pre-normative research program DUSTINANO CEN Mandate
189 M/461 for dustiness of nanomaterial powders ^[52]. Some of the powder properties obtained in
190 the characterization task of this project are gathered in **Table 1** with indications of their major
191 applications. These powders are used in several areas, from chemical industry applications to
192 building, cosmetics and food. Typical SEM micrographs of each material are shown. It can be
193 seen that the powders studied are composed of aggregates of spherical constituent particles
194 covering a range of particle sizes from 7 nm to 36 nm determined from SEM images analysis.

195

196
197

Table 1: Characteristics of the powders studied in this work for the demonstration of equivalence between powder external specific surface area and collected particles external specific surface area (data from [52]).

Powder	TiO ₂ (b)	TiO ₂ (d)	SiO ₂ (a)	SiO ₂ (b)	BaSO ₄ (b)
A _{Ex} (m ² /g)	55	140	92	240	38
Particle size (nm)	20	10	35	15	36
Applications	Food & Cosmetics	Cosmetics (Solar creams)	Food (anti-agglomerate) & Cosmetics	Pharmaceutics & Cosmetics (anti-agglomerate)	Catalysis and whitening agent

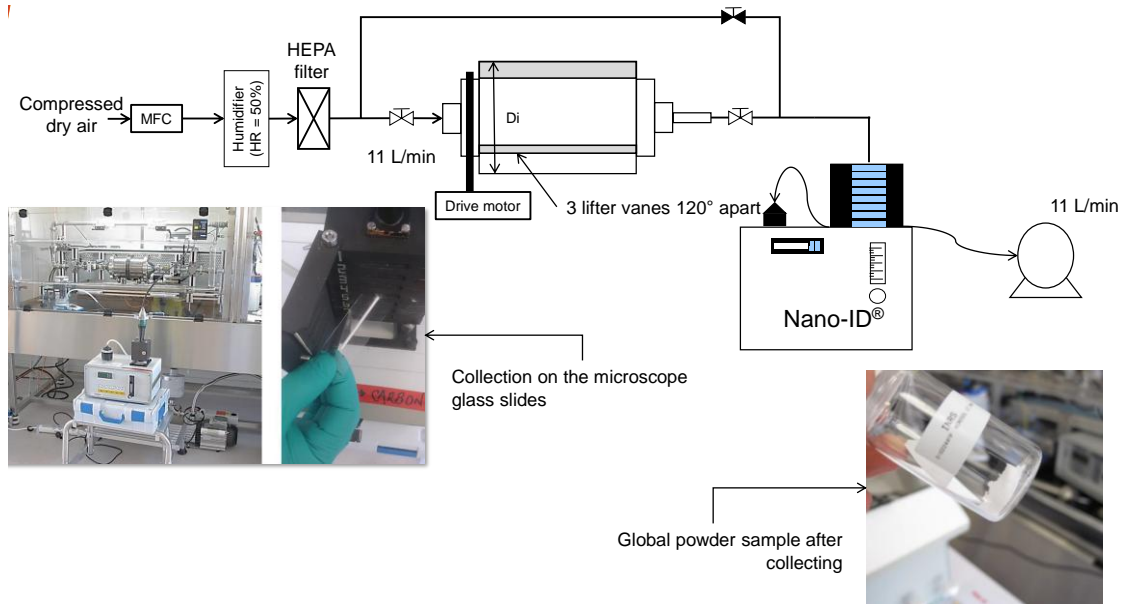
198

199

200
201
202
203
204

3.3. Aerosol generation and sampling

Figure 2 shows the set-up implemented for aerosol generation and aerosol sampling. It involves a Small Rotating Drum (SRD) dustiness test bench as aerosol generation system coupled with a cascade impactor for aerosol sampling.



205
206

Figure 2: Set-up of the aerosol sampling step.

207 The SRD system is a stainless steel drum (internal diameter 16.3 cm; volume 5.93 L) rotating
208 following its horizontal axis at a constant speed (11 rpm). Three lifter vanes at 120° apart are
209 positioned inside the drum. When the drum rotates, the lifter vanes carry up roughly 6 g of
210 powder sample previously spread along the lifter vane, causing a drop inside the drum and
211 create the aerosol. The aerosol is transferred by a horizontal airflow ($V = 0.9 \text{ cm}\cdot\text{s}^{-1}$)
212 conditioned at 50% relative humidity and filtered (HEPA) from the exit drum cone to the
213 sampling device.

214 The cascade impactor used is a Nano-ID[®] apparatus equipped with microscope glass slides on
215 each stage to collect the particles with a dry process. This impactor was fully described by
216 Gorbunov et al. [53]. It was not implemented to determine the particle size distribution; the sole
217 objective was to collect as much as possible aerosolized particles to have enough matter for
218 further off-line gas adsorption measurements ($A_{\text{Ex}(\text{collected particles})}$). To this end, the diffusion
219 battery associated with the Nano-ID[®], situated at the outlet of the impactor, was not used.
220 Indeed, preliminary tests showed the absence of particles under 0.25 μm aerodynamic
221 diameter. For each powder, the aerosol generation with the SRD lasted three minutes as
222 described in the standard but the SRD rotation was repeated between five and ten times on

223 the same sample mass (6 g) inside the drum to collect and cumulate enough matter to be
224 analyzed by gas adsorption as explained above. After aerosolization, the global powder
225 samples collected after gathering each of the impactor stages totalized a mass between 40 and
226 300 mg of aerosolized powder, which was estimated compatible with further gas adsorption
227 analysis.

228

229 **3.4. Gas adsorption**

230 Gas adsorption measurements on both the powder and aerosol samples were performed in
231 triplicates with an adsorption manometer (ASAP 2020 Plus, Micromeritics) with nitrogen
232 (N₂) as gas probe at 77K. The powder samples were outgassed under vacuum (10⁻² mmHg) at
233 150°C during a minimum of 12 hours. This preparation is required before gas adsorption
234 measurement to limit underestimated calculated external specific surface area values ^[54]. The
235 BET model was applied to determine the external specific surface area for non-porous,
236 macroporous or mesoporous powders characterized by a type II or type IV isotherm, whereas
237 the t-plot model was used for microporous powders characterized by a type I isotherm
238 according to the IUPAC recommendation ^[45].

239

240 Finally, the error for the surface-based dustiness index was obtained following the error
241 propagation law related to a product:

242

$$\Delta DI_s = DI_M \times \Delta A_{ex(\text{collected particles})} + \Delta DI_M \times A_{ex(\text{collected particles})}$$

243 With ΔDI_M the error for 3 replicates on the DI_M and $\Delta A_{ex(\text{collected particles})}$ the error for 3
244 replicates on the $A_{ex(\text{collected particles})}$

245

246

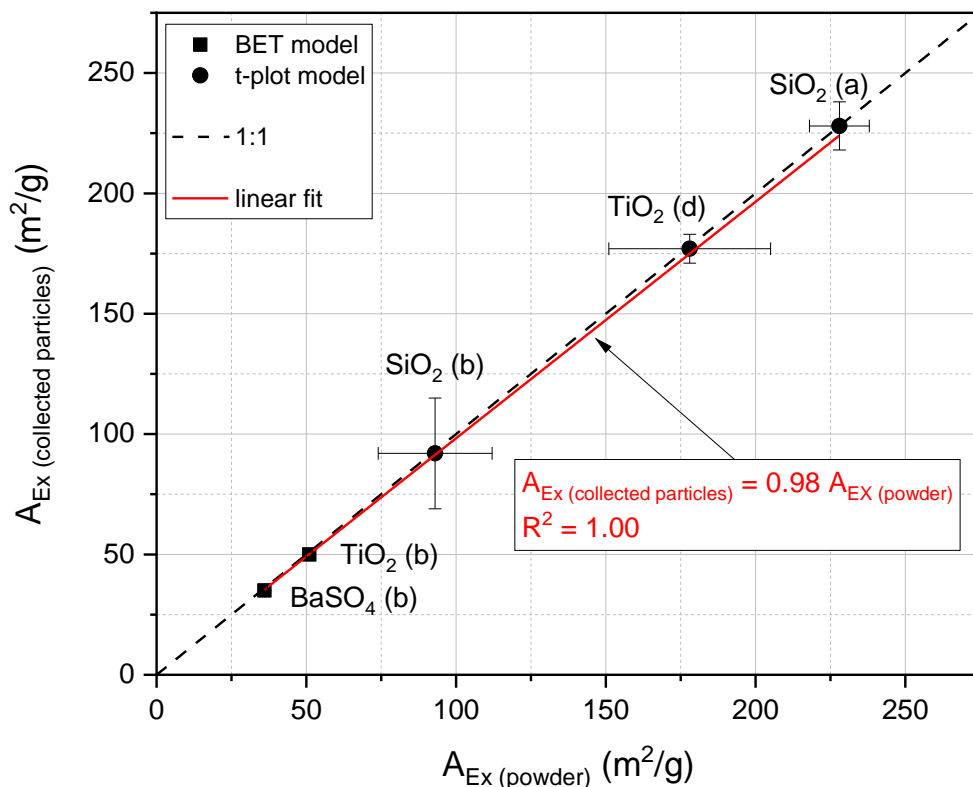
247 **4. Results and Discussion**

248 **4.1. Comparison of $A_{Ex(\text{powder})}$ and $A_{Ex(\text{collected particles})}$**

249 On **Figure 3**, specific surface areas obtained for both the powder and the aerosols are
250 compared ($A_{Ex(\text{powder})}$ and $A_{Ex(\text{collected particles})}$, respectively). The values are represented with
251 one standard deviation. The external specific surface areas cover almost one order of
252 magnitude, from 35 to 228 m².g⁻¹ in terms of powder A_{Ex} .

253 BaSO₄ (b) and TiO₂ (b) are non-porous powders characterized by a type II isotherm both for
254 the powders and the aerosolized samples. Therefore, the BET model was applied to determine
255 the $A_{Ex(\text{powder})}$ and $A_{Ex(\text{collected particles})}$ for these materials. For SiO₂ (b), TiO₂ (d) and SiO₂ (a),

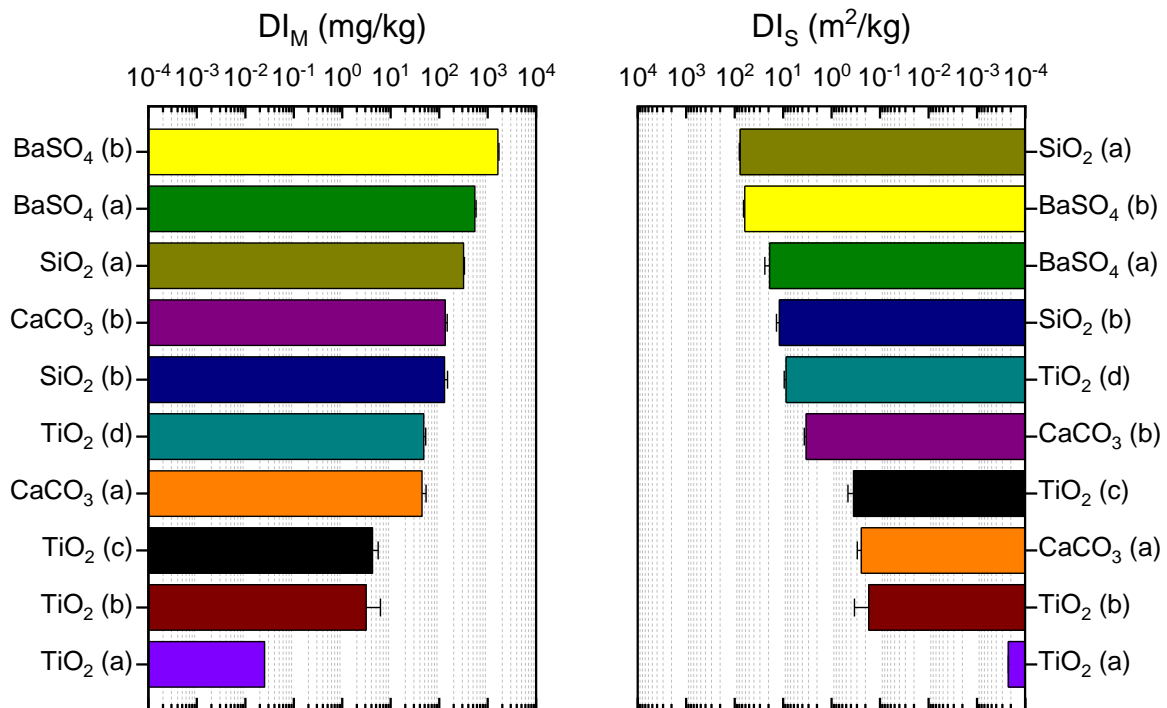
256 type II and type I composite isotherms were obtained for the powders and the aerosolized
 257 samples. In these cases, the t-plot model was applied to distinguish the external $A_{\text{Ex (powder)}}$ and
 258 $A_{\text{Ex (collected particles)}}$ from the internal surface. Finally, a consistent correlation ($R^2 = 0.99$)
 259 between $A_{\text{Ex (collected particles)}}$ and $A_{\text{Ex (powder)}}$ is observed.
 260 These results demonstrate the equivalence between $A_{\text{Ex (powder)}}$ and $A_{\text{Ex (collected particles)}}$; this
 261 finding allows the surface-based dustiness index to be calculated with the sole $A_{\text{Ex (powder)}}$ as
 262 stated in Equation 2. Differences observed between $A_{\text{Ex(powder)}}$ and $A_{\text{Ex(collected particles)}}$ would
 263 have suggested that the powder-borne particles are modified by the mechanical process during
 264 the dustiness test (e.g. entailing, attrition, melting), affecting their external surface area. Given
 265 the stability of surface areas measured through this experimental approach, it is reasonable to
 266 assume that this relationship is transferable to the RD and CD, as these are based on the same
 267 mechanical process (drop or drop + rotation) as the small drum. .



268
 269 **Figure 3:** Comparison between external specific surface area of powders and aerosols. The error bars correspond to one
 270 standard deviation ($n = 3$).

271
 272 **4.2. Application of the surface-based dustiness index to a series of nanomaterial**
 273 **powders**

274 The proposed surface-based dustiness index as described in equations 1 and 2 was applied to a
 275 data set from different works implying the mass-based dustiness index determination and a
 276 powder characterization providing $A_{Ex(\text{powder})}$ [52, 55-56]. The mass-based dustiness indices were
 277 obtained with the VS method in the work from Dazon et al. [55], whereas the data from the
 278 CEN project were obtained with the Rotating Drum (RD) method according to the
 279 standardized protocol [52]. All the powders in the aforementioned works are characterized by
 280 more or less polydispersity and a monomodal distribution.
 281 On **Figure 4** powders of the CEN DUSTINANO [52] project are ranked according to surface-
 282 based and mass-based dustiness indices in the respirable fraction after the RD tests.
 283



284
 285 **Figure 4:** Comparison between the surface-based and mass-based dustiness indices in terms of ranking for a series of
 286 manufactured powders studied in the CEN DUSTINANO European project Commission Mandate M/461 in the respirable
 287 fraction after RD tests (data from [52]). The error bars correspond to one standard deviation ($n = 3$)

288 On **Figure 4**, we highlight that the surface-based dustiness index DI_S is more sensitive than
 289 the mass-based dustiness index DI_M with one extra order of magnitude covered from 10^{-4} to
 290 $10^2 \text{ m}^2.\text{kg}^{-1}$ compared to a range from 10^{-2} to $10^3 \text{ mg}.\text{kg}^{-1}$ for the DI_M . This result suggests that
 291 the surface-based dustiness index DI_S allows distinguish powders better than the mass-based
 292 one. For instance, CaCO_3 (b) and SiO_2 (b) have very close DI_M . Taking into account the
 293 standard deviations, these two powders can be considered as dusty as the other. With the

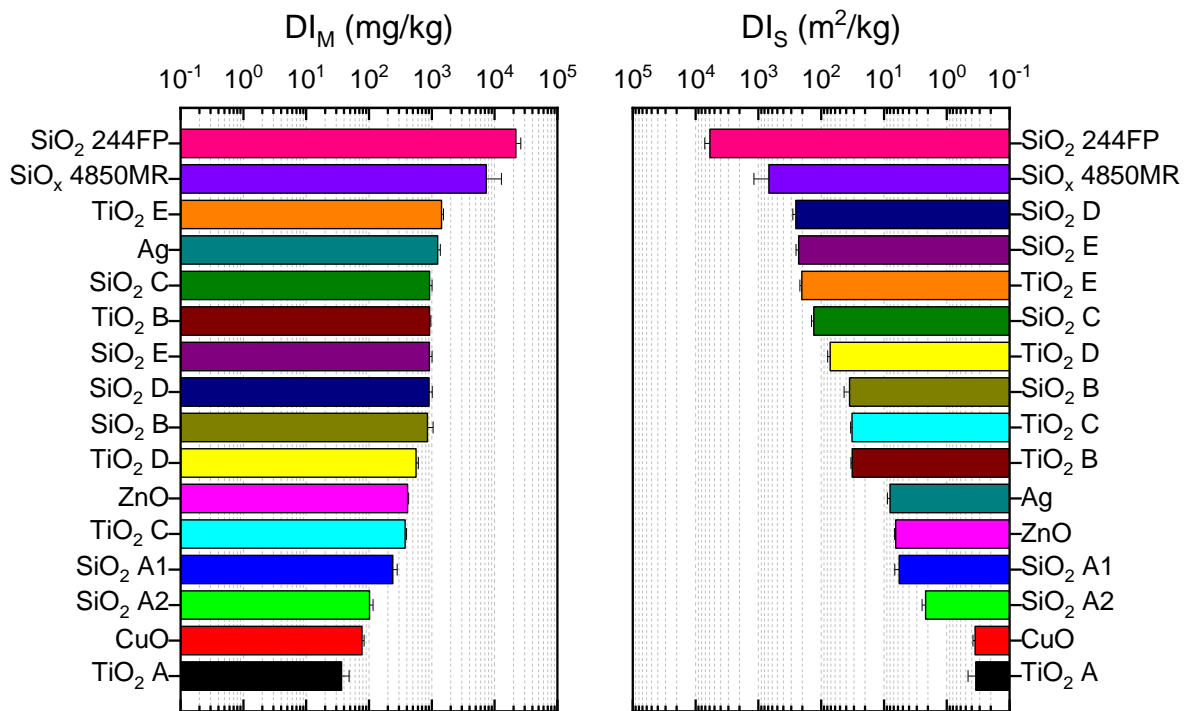
294 surface metric, SiO₂ (b) is clearly dustier than CaCO₃ (b). In terms of impact on a risk
295 assessment implying the use of dustiness data and ranking, the preventative measures
296 regarding the SiO₂ (b) may not be the same that those for the CaCO₃ (b). In a safe-by-design
297 concept, it could be suggested for instance to substitute the SiO₂ (b) by a less dusty powder if
298 possible, provided that the properties of the both powders are similar and compatible with the
299 final application. As previously stated, the RD method should not modify the individual
300 particle shape and size, and by extension the surface area, allowing the surface-based
301 dustiness to be calculated. Even in case of bimodal distributions, or composite materials, the
302 surface area is linked to an average size, and should not be impacted. The surface area is an
303 integral parameter that does not inform about particle size distribution, nor the composite
304 nature of the particles. Such information shall be known before performing a dustiness test, as
305 recommended by the different standards. In this study, the powders are almost of similar
306 nature and morphology, and do allow highlight relationships between the surface-based
307 dustiness metric and their intrinsic physico-chemical properties. Moreover, it remains unclear
308 what set of particles properties are the most relevant to be taken into account in the
309 framework of risk management. As stated by Maynard & Aitken ^[57], in the absence of
310 unequivocal relationships involving a given parameter, the combination of multiple exposure
311 metrics and particle properties remains necessary.

312 Another interesting result with the surface-based dustiness index is the powder ranking.
313 Generally speaking, materials displaying low specific surface-area $A_{Ex(powder)}$, and then coarser
314 particles decrease in the ranking with the DI_S whereas the contrary is obtained for the mass-
315 based approach. This result theoretically expected, reinforces the need to use several metrics
316 when implementing risk assessment. The number-based dustiness index can also support this
317 observation since the powder ranking follows the same path as the surface-based DI, with
318 smaller particles in the powder increasing the dustiness index, as demonstrated in recent
319 works ^[56]. Here, the TiO₂ (d) characterized by a higher specific surface area than the CaCO₃
320 (a) (142 m².g⁻¹ for TiO₂ (d) vs 5.5 m².g⁻¹ for CaCO₃ (a)) increases by one position with the
321 DI_S compared to the mass-based metric, whereas it is the contrary for the calcium carbonate
322 powder. The ranking modifications between mass-based and surface-based dustiness indices
323 could have an impact on the risk assessment management. Currently, the mass-based
324 dustiness index is the reference to implement risk assessment in workplaces where powders
325 are handled, but if the surface metric is to be confirmed more relevant, a new approach
326 including both metrics in dustiness tests could be developed, in particular, substances for
327 which a dose-response is recognized and/or for hazardous materials for environment safety.

328

329 Similarly to **Figure 4**, the powder dustiness ranking according to both surface- and mass-
330 based dustiness indices from Dazon et al. [55] are displayed in **Figure 5**. In the actual case of
331 the VS method, the surface-based dustiness index also leads to a better distinction between
332 materials: the DI_S cover one extra order of magnitude compared to the DI_M ones. For instance,
333 the SiO_2 B and D have very close DI_M . Modifying the mass-based by the surface-based
334 dustiness index, SiO_2 B clearly becomes less dusty than SiO_2 D. The very close surface areas
335 obtained before and after aerosolization with the VS method confirmed that the vortex does
336 not influence the particle size distribution and let apply the relationship we propose for the
337 surface based dustiness index.

338 These results strengthen the relevancy to characterize the dustiness based on a surface metric,
339 and this for a variety of industrial powders, characterized by a reduced polydispersity and
340 similar chemical compositions. Taking into account the possible importance of surface area
341 characterization, in particular in toxicological studies, a surface-based dustiness index could
342 bring interesting information to document the powders under study in such research area.
343 Moreover, the surface-based metric appears complementary to the mass and number-based
344 dustiness indices indicated in the current standards since it proposes kind of compromise, the
345 number-based dustiness index being strongly influenced by the smallest particles.



346

347 **Figure 5:** Comparison between the surface-based and mass-based dustiness indices in terms of ranking for a series of
348 manufactured powders studied in the INRS research program (data from [55-56]). The error bars correspond to one standard
349 deviation (n = 3).

350 **5. Conclusion**

351 In this study, we describe an operational methodology that leads us to propose a surface-based
352 dustiness index (DI_S) and an associated determination methodology. This index involves both
353 the reference mass-based dustiness index (DI_M) and the specific surface area of the aerosol.
354 The equivalence between external specific surface area of powders and their aerosols was
355 therefore first demonstrated with five representative industrial nanopowders in a range of
356 external specific surface areas from 35 to 230 $m^2 \cdot g^{-1}$.

357 The results presented here show that the DI_S allows a better distinction between powders in
358 terms of dustiness indices, and covers an additional order of magnitude compared to the DI_M .
359 In addition, the classification of powders is modified according to the metric considered in the
360 dustiness index, either on a mass or surface basis. This re-organization of the classification of
361 powders according to their degree of dustiness could have an impact on the assessment of the
362 associated risks, with new adaptation measures proposed depending on the nanomaterial
363 handled in the workplace. If the DI_S proves its reliability for the assessment of pulmonary
364 toxicity of insoluble or poorly soluble nanomaterials, DI_S could be included in the ongoing
365 revisions of European standards for dustiness measurements of nanomaterial powders.
366 Moreover, environmental safety could benefit from these results on surface area dustiness
367 metric, since it could be a relevant parameter for preventing dust explosions and managing
368 safety in industrial facilities. This study, although based on preliminary results, should
369 stimulate research on dustiness measurement addressing t environmental risks in this
370 perspective. However, , further investigations are needed with other nanomaterial and non-
371 nanomaterial powders, extending the applicability domain limited for the moment to the same
372 type of materials studied here, as well as with other dustiness measurement methods than the
373 ones used here for demonstration (Rotating Drum and Vortex Shaker) to confirm the added
374 value for the whole nanosafety research community.

375

376 **Acknowledgements**

377 This work was supported by the European Commission, as part of the contract
378 SA/CEN/ENTR/461/2012-06, Mandate M/461 ‘Standardisation activities regarding
379 nanotechnologies and nanomaterials’.

380

381 **Authors contributions**

382 Claire Dazon: Proposition, writing draft and final article; organisation and implementation of
383 aerosol experiments, data analysis

384 Sébastien Bau: Reviewing article, implementation of aerosol experiments
385 Raphaël Payet: Implementation of aerosol experiments
386 Vanessa Fierro: Reviewing article, implementation of gas adsorption experiments
387 Olivier Witschger: member of the CEN project Mandate M/461 organizer, experimental
388 supervision, collecting SEM analysis data, article reviewing

389

390 **Conflict of Interest**

391

392 The authors declare no conflict of interest.

393

394 **References**

395 [1] G. Fytianos, A. Rahdar, G. Z. Kyzas, Nanomaterials in Cosmetics: Recent Updates
396 *Nanomaterials*, 2020, **10**, 979.

397 [2] R.B. Peters, H. Bouwmeester, S. Gottardo, V. Amenta, M. Arena, P. Brandhoff, H.J.P.
398 Marvin, A. Mech, F. Botelho Moniz, L. Quiros Pseudo, H. Rauscher, R. Schoonjans, A. K.
399 Undas, M. V. Vettori, S. Weigel, K. Aschberger, Nanomaterials for products and application
400 in agriculture, feed and food, *Trends in Food Science & Technology*, 2016, **54**, 155-164.

401 [3] I. Hincapié, A. Caballero-Guzman, D. Hiltbrunner, B. Nowack, Use of engineered
402 nanomaterials in the construction industry with specific emphasis on paints and their flows in
403 construction and demolition waste in Switzerland, *Waste Management*, 2015, **43**, 398-406.

404 [4] F. Piccinno, F. Gottschalk, S. Seeger, B. Nowack, Industrial production quantities and
405 uses of ten engineered nanomaterials in Europe and the world, *Journal of Nanoparticle*
406 *Research*, **2012**, 14, 1109.

407 [5] Ministère de la Transition Ecologique et Solidaire (**2020** Report on the declaration of
408 substances imported, manufactured or distributed in France in 2019) available to
409 <http://www.r-nano.fr>.

410 [6] H. Kangas and M. Pitkänen, in *Industrial Applications of Nanomaterials Micro and Nano*
411 *Technologies*, (Eds: S. Thomas, Y. Grohens, Y. B. Pottathara), Elsevier Inc, **2019**, Ch.1.

412 [7] M. Debia, B. Bakhiyi, C. Ostiguy, J.H. Verbeek, D.H. Brouwer, V. Murashov, A
413 Systematic Review of Reported Exposure to Engineered Nanomaterials, *The Annals of*
414 *Occupational Hygiene*, 2016, **60**, 916-935.

415 [8] T. Kuhlbusch, C. Asbach, H. Fissan, D. Gohler, M. Stintz, Nanoparticle exposure at
416 nanotechnology workplaces: A review, *Toxicology*, 2011, **8**, 22.

- 417 [9] D. Brouwer, Exposure to manufactured nanoparticles in different workplaces, *Toxicology*,
418 2010, **269**, 120-127.
- 419 [10] O. Witschger, O. Le Bihan, M. Reynier, C. Durand, A. Marchetto, E. Zimmerman, D.
420 Charpentier, Nanomaterials definition: Identification and Characterization of Materials and
421 Associated Professional Exposures, *Hygiène et Sécurité du Travail*, 2012, **ND 2355**, 41-55.
- 422 [11] M. Methner, L. Hodson and C. Geraci, Nanoparticle emission assessment technique
423 (NEAT) for the identification and measurement of potential inhalation exposure to engineered
424 nanomaterials – part A., *Journal of Occupational and Environmental Hygiene*, 2010, **7**, 127-
425 132.
- 426 [12] M. Methner, L. Hodson, A. Dames and C. Geraci, Nanoparticle emission assessment
427 technique (NEAT) for the identification and measurement of potential inhalation exposure to
428 engineered nanomaterials – part B: results from 12 field studies., *Journal of Occupational and
429 Environmental Hygiene*, 2010, **7**, 163-176.
- 430 [13] A. C. Eastlake, C. Beaucham, K. F. Martinez, M. M. Dahm, C. Sparks, L. L. Hodson and
431 C. L. Geraci, Refinement of the Nanoparticle Emission Assessment Technique into the
432 Nanomaterial Exposure Assessment Technique (NEAT 2.0). *Journal of Occupational and
433 Environmental Hygiene*, 2016, **13**, 708-717.
- 434 [14] S.J. Froggett, S.F. Clancy, D.R. Boverhof, R.A. Canady. A review and perspective of
435 existing research on the release of nanomaterials from solid nanocomposites, *Part. Fibre Tox.*,
436 2014, **11**, 17.
- 437 [15] N. Halil, R. Rusli, M. Z. Abidin, S. Jamen, F. Khan, An integrated health risk assessment
438 with control banding for nanomaterials exposure, *Process Saf Prog.*, 2022, **41**, S84–S97.
- 439 [16] E. Kuijpers, C. Bekker, D. Brouwer, M. le Feber, W. Fransman, Understanding workers'
440 exposure: Systematic review and data-analysis of emission potential for NOAA, *Journal of
441 Occupational and Environmental Hygiene*, 2017, **14**, 349-359.
- 442 [17] C. Bekker, E. Kuijpers, D.H. Brouwer, R. Vermeulen, W. Fransman, Occupational
443 Exposure to Nano-Objects and Their Agglomerates and Aggregates Across Various Life
444 Cycle Stages; A Broad-Scale Exposure Study, *The Annals of Occupational Hygiene*, 2015, **59**,
445 681-704.
- 446 [18] G. Lidén, Dustiness Testing of Materials Handled at Workplaces, *The Annals of
447 Occupational Hygiene*, 2006, **50**, 437-439.
- 448 [19] K.H. Dunn, A.C. Eastlake, M. Story, E.D. Kuempel, Control banding tools for
449 engineered nanoparticles : what the practitioner needs to know, *Annals of Work Exposures
450 and Health*, 2018, **62**, 362-388.

451 [20] J. Sánchez Jiménez, C. Varet, G.J. Poland, S.M. Fern, S.M. Hankin, M. van Tongeren, A
452 comparison of control banding tools for nanomaterials, *Journal of Occupational and*
453 *Environmental Hygiene*, 2016, **13**, 936-949.

454 [21] B. Van Duuren-Stuurman, S. R. Vink, K. J. M. Verbist, H. G. A. Heussen, D. H.
455 Brouwer, D. E. D. Kroese, M. F. J. van Niftrik, E. Tielemans, W. Fransman, Range-finding
456 risk assessment of inhalation exposure to nanodiamonds in a laboratory environment, *The*
457 *Annals of Occupational Hygiene*, 2012, **56** (5), 525–541.

458 [22] W. Fransman, M. van Tongeren, J. Cherrie, M. Tischer, T. Schneider, J. Schinkel, H.
459 Kromhout, N. Warren, H. Goede, E. Tielemans, Advanced Reach Tool (ART) : development
460 of the mechanistic model, *The Annals of Occupational Hygiene*, 2011, **55**, 957-979.

461 [23] S.F. Hansen, S.N. Sørensen, L.M. Skjolding, N.B. Hartmann, A. Baun, Revising REACH
462 guidance on information requirements and chemical safety assessment for engineered
463 nanomaterials for aquatic ecotoxicity endpoints: recommendations from the EnvNano,
464 *Environmental Sciences Europe*, 2017, **29**, 14.

465 [24] A. Klippel, M. Schmidt, U. Krause, Dustiness in workplace safety and explosion
466 protection: Review and outlook, *Journal of Loss Prevention in the Process Industries*, 2015,
467 **34**, 22-29.

468 [25] EN 17199-1 (2019a) Workplace exposure - Measurement of dustiness of bulk materials
469 that contain or release respirable NOAA or other respirable particles - Part 1: Requirements
470 and choice of test methods.

471 [26] EN 17199-2 (2019b) Workplace exposure - Measurement of dustiness of bulk materials
472 that contain or release respirable NOAA or other respirable particles - Part 2: Rotating Drum
473 method.

474 [27] EN 17199-3 (2019c) Workplace exposure - Measurement of dustiness of bulk materials
475 that contain or release respirable NOAA or other respirable particles - Part 3: Continuous
476 Drop method.

477 [28] EN 17199-4 (2019d) Workplace exposure - Measurement of dustiness of bulk materials
478 that contain or release respirable NOAA or other respirable particles - Part 4: Small Rotating
479 Drum method.

480 [29] EN 17199-5 (2019e) Workplace exposure - Measurement of dustiness of bulk materials
481 that contain or release respirable NOAA or other respirable particles - Part 5: Vortex Shaker
482 method.

483 [30] CEN (1993). "Workplace atmospheres - Size fraction definitions for measurement of
484 airborne particles. EN 481."

- 485 [31] C. Ribalta, A. J. Koivisto, A. López-Lilao, S. Estupiñá, M. C. Minguillón, E. Monfort, M.
486 Viana, Testing the performance of one and two box models as tools for risk assessment of
487 particle exposure during packing of inorganic fertilizer, *Science of the Total Environment*,
488 2019, **650**, 2423–2436.
- 489 [32] C. Ribalta, A. López-Lilao, S. Estupiñá, A.S. Fonseca, A. Tobías, A. García-Cobos, M.C.
490 Minguillón et al., Health risk assessment from exposure to particles during packing in
491 working environments, *Science of the Total Environment*, 2019, **671**, 474–487.
- 492 [33] C. Ribalta, M. Viana, A. López-Lilao, S. Estupiñá, M. C. Minguillón, J. Mendoza et al.,
493 On the Relationship between Exposure to Particles and Dustiness during Handling of Powders
494 in Industrial Settings, *Annals of Work Exposures and Health*, 2019, **63** (1), 107–123.
- 495 [34] C. Ribalta, A. López-Lilao, A.S. Fonseca, A.C.Ø. Jensen, K.A Jensen, E. Monfort, M.
496 Viana, *Toxics*, Evaluation of One- and Two-Box Models as Particle Exposure Prediction
497 Tools at Industrial Scale, 2021, **9**, 201.
- 498 [35] K.A. Roach, S.E. Anderson, A.B. Stefaniak, H.L. Shane, V. Kodali, M. Kashon, J.R.
499 Roberts, Surface area- and mass-based comparison of fine and ultrafine nickel oxide lung
500 toxicity and augmentation of allergic response in an ovalbumin asthma model, *Inhalation*
501 *Toxicology*, 2019, **31** (8), 299-324.
- 502 [36] O. Schmid and T. Stoeger, Surface area is the biologically most effective dose metric for
503 acute nanoparticle toxicity in the lung, *Journal of Aerosol Science*, 2016, **99**, 133-143.
- 504 [37] NIOSH (2011) Occupational exposure to titanium dioxide, Current intelligence bulletin,
505 n°63, 119 p.
- 506 [38] F. Cosnier, C. Seidel, S. Valentino, O. Schmid, S. Bau, U. Vogel, J. Devoy and L. Gaté,
507 Retained particle surface area dose drives inflammation in rat lungs following acute, subacute,
508 and subchronic inhalation of nanomaterials, *Particle and Fibre Toxicology*, 2021, **18** (1): 29.
- 509 [39] R. Duffin, C. L. Tran, A. Clouter, D. M. Brown, W. MacNee, V. Stone, K. Donaldson,
510 The Importance of Surface Area and Specific Reactivity in the Acute Pulmonary
511 Inflammatory Response to Particles, *The Annals of Occupational Hygiene*, 2002, **46** (1): 242-
512 245
- 513 [40] G. Oberdörster, E. Oberdörster, J. Oberdörster, Nanotoxicology: an emerging discipline
514 evolving from studies of ultrafine particles, *Environmental Health Perspectives*, 2005, **113**
515 (7): 823-39.
- 516 [41] T. Stoeger, C. Reinhard, S. Takenaka, A. Schroepel, E. Karg, B. Ritter, J. Heyder, and
517 H. Schulz, Instillation of Six Different Ultrafine Carbon Particles Indicates a Surface Area

518 Threshold Dose for Acute Lung Inflammation in Mice, *Environmental Health Perspectives*,
519 2006, **114** (3): 328-333.

520 [42] P. McGarry, S. Clifford, L. D. Knibbs, C. He and L. Morawska, Application of multi-
521 metric approach to characterization of particle emissions from nanotechnology and non-
522 nanotechnology processes, *Journal of Occupational and Environmental Hygiene*, 2016, **13**
523 (10), D175-D197.

524 [43] V.A. Hackley and A. B. Stefaniak, “Real-world” precision, bias, and between-laboratory
525 variation for surface area measurement of a titanium dioxide nanomaterial in powder form,
526 *Journal of Nanoparticle Research*, 2013, **15** (6), 1742.

527 [44] S. Brunauer, P.H. Emmet, E. Teller, Adsorption of Gases in Multimolecular Layers,
528 *Journal of the American Chemical Society*, 1938, **60**, 309-319.

529 [45] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J.
530 Rouquerol, K.S.W. Sing, Physisorption of Gases, with Special Reference to the Evaluation of
531 Surface Area and Pore Size Distribution, *IUPAC Technical Report*, 2015, **87** (9-10): 1051-
532 1069.

533 [46] S. Bau, C. Dazon, O. Rastoix, N. Bardin-Monnier, Effect of constituent particle
534 polydispersion on VSSA-based equivalent particle diameter: Theoretical rationale and
535 application to a set of eight powders with constituent particle median diameters ranging from
536 9 to 130 nm, *Adv. Powder Tech.* 2021, **32** (5): 1369-1379.

537 [47] S. Bau, B. Zimmermann, R. Payet and O. Witschger, S. Bau, B. Zimmermann, R. Payet
538 and O. Witschger, A laboratory study of the performance of the handheld diffusion size
539 classifier (DiSCmini) for various aerosols in the 15–400 nm range, *Environmental Science:*
540 *Processes and Impacts*, 2015, **17**, 261-269.

541 [48] M. Levin, O. Witschger, S. Bau, E. Jankowska, I. K. Koponen, A. J. Koivisto, P. A.
542 Clausen, A. Jensen, K. Molhave, C. Asbach and K. A. Jensen, Can We Trust Real Time
543 Measurements of Lung Deposited Surface Area Concentrations in Dust from Powder
544 Nanomaterials?, *Aerosol And Air Quality Research*, 2016, **16**, 1105-1117.

545 [49] R.F. Lebouf, A.B. Stefaniak, B.T. Chen, D.G. Frazer, M.A. Virji, Measurement of
546 airborne nanoparticle surface area using a filter-based gas adsorption method for inhalation
547 toxicology experiments, *Nanotoxicology*, 2011, **5**, 687-699.

548 [50] S. Bau, O. Witschger, F. Gensdarmes, O. Rastoix, D. Thomas, A TEM-based method as
549 an alternative to the BET method for measuring off-line the specific surface area of
550 nanoaerosols, *Powder Tech.*, 2010, **200**, 190-201.

551 [51] S. Bourrous, Q. Ribeyre, L. Lintis, J. Yon, S. Bau, D. Thomas, C. Vallières and F.-X.
552 Ouf, A semi-automatic analysis tool for the determination of primary particle size, overlap
553 coefficient and specific surface area of nanoparticles aggregates, *Journal of Aerosol Science*,
554 2018, **126**, 122-132.

555 [52] O. Witschger, C. Dazon, R. Payet, S. Bau, A. Boivin, O. Deloras, Workplace exposure -
556 Measurement of dustiness of bulk nanomaterials - Part 1 to Part 5 Deliverable Report on the
557 results of pre-normative research, 2016, 111 p.

558 [53] B. Gorbunov, N. D. Priest, R. B. Muir, P. R. Jackson, H. Gnewuch, A Novel Size-
559 Selective Airborne Particle Size Fractionating Instrument for Health Risk Evaluation,*The*
560 *Annals of Occupational Hygiene.*, 2009, **53**, 225–237.

561 [54] J. Rouquerol, F. Rouquerol, M. Triaca, O. Cerclier, The use of thermal analysis to select
562 the standard outgassing conditions of a set of reference adsorbents, *Thermochimica Acta*,
563 1985, **85**, 311-314.

564 [55] C. Dazon, *PhD Thesis*, Aix-Marseille University, France, 2019.

565 [56] O. Witschger and C. Dazon, Dustiness of nanomaterials : outlook of the existing research
566 and perspectives, *Hygiène et Sécurité du Travail*, 2019, **256**, 41-47.

567 [57] A. D. Maynard & R. J. Aitken Stoeger, Assessing exposure to airborne nanomaterials:
568 Current abilities and future requirements, *Nanotoxicology*, 2007, **1:1**, 26-41.

569