Exposure to nanomaterials in Germany

Bundesanstalt für Arbeitsschutz und Arbeitsmedizin

Results of the corporate survey of the Federal Institute for Occupational Health and Safety (BAuA) and the Association of the Chemical Industry (VCI) using questionnaires

1 Introduction

Starting points for the joint questionnaire campaign were the stakeholder dialog events on 26 September 2005 at VCI in Frankfurt and on 11/12 October 2005 at the German Federal Ministry for the Environment (BMU) in Bonn. Public authorities and industry saw a need for information regarding the manufacture and handling of nanomaterials at the workplace. For this reason, BAuA and VCI agreed to jointly gather relevant data, using a questionnaire format for this purpose.
The campaign aimed to improve the data situation for activities involving the handling of synthetic nanomaterials. This enables the identification of focal fields, their targeted coverage and the issuing of recommendations for effective protection measures [1; 2].
Preparations were carried out and contents of the questionnaire were agreed in consensus with an accompanying working group of delegates from BAuA, VCI and the chemical industry. The questionnaire developed by the WG can be accessed under
www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/Nanotechnology/Nanotechnology.html

The questionnaire consists of two parts:
- a "general part" with general, cross-product questions, and
- a "specific part" with product-specific questions on individual nanomaterials.

The questionnaire was sent to a total of 656 companies. In a first round VCI contacted 150 of its member companies; in a second round BAuA contacted 506 member companies of the Federation of German Industries (BDI) and start-up companies, respectively, based on a list of the German Federal Ministry of Education and Research (BMBF). VCI received and anonymized returned questionnaires. Data were checked and evaluated by BAuA.

That was the start of the first questionnaire campaign in Germany regarding activities involving nanomaterials.

2 Results

217 companies took part in the questionnaire campaign, so that a return rate of 33% was achieved. It emerged that 79% of companies do not perform any activities involving nanomaterials, according to the definition and starting criterion of the questionnaire. With the questionnaire-specific definition "Synthetic nanoparticles in the meaning of this questionnaire are particles manufactured as powders which have, in at least two dimensions, an extension of under 0.1 µm, as well as their aggregates and agglomerates ..." the emphasis of the campaign was placed expressly on potential exposure by inhalation. But this approach excluded nanomaterials which are produced or processed from suspensions.

Furthermore, the starting criterion for the questionnaire was "activities involving nanomaterials (production, use or processing) from 10 kg/year". In retrospect, this volume turned out to be too high in the establishment of this novel and "lightweight" technology, where work at laboratory scale is still characteristic.

Thus 21% of companies (n=45) perform activities involving nanomaterials (see fig. 1), according to the criteria of the questionnaire.

2.1 General part of the questionnaire

Activities involving nanomaterials are essentially characterized by use (12%; n=26) and production and use (6%; n=13). Only 1% of companies (n=2) can be seen purely as producers (see fig. 1).

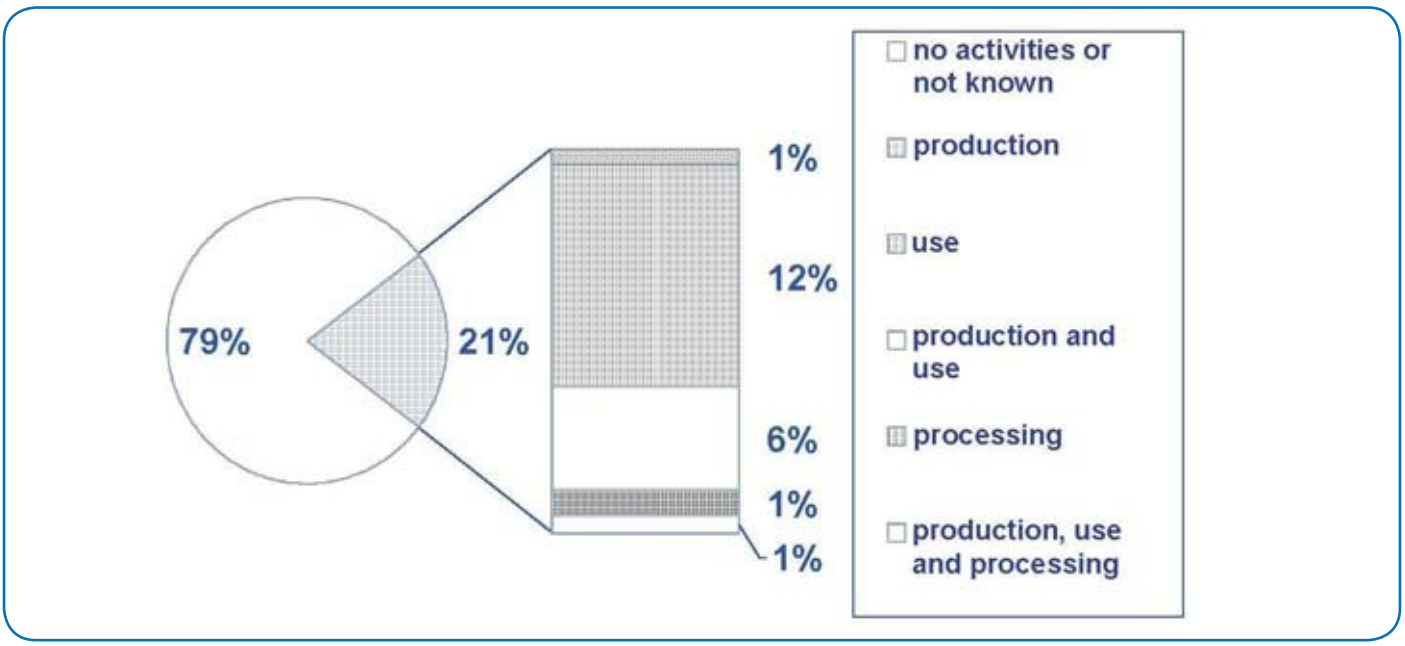

Fig. 1 Companies with activities involving nanomaterials

Most companies (40%; n=18) carry out activities involving nanomaterials in rather small volumes of only 10 to 100 kg per annum. When adding companies with volumes of < 10 kg/year (who responded ignoring the starting criterion of > 10 kg/year), this share increases to 51% (n=23). It can be assumed that this share would have been even higher without the given starting criterion. By contrast, only 11% of companies (n=5) produce nanomaterials in volumes of over 100 tons/year.

Fig. 2 shows annual levels of activities involving nanomaterials, broken down by VCI and BDI member companies, respectively. It emerges that especially companies who handle nanomaterials in volumes of < 100 kg/year are BDI members and, most probably, fall in the group of start-ups (see fig. 2)[1] . With larger company sizes, the number of VCI members increases. Companies with annual activities involving nanomaterials in volumes of > 1000 tons/year are exclusively VCI members.

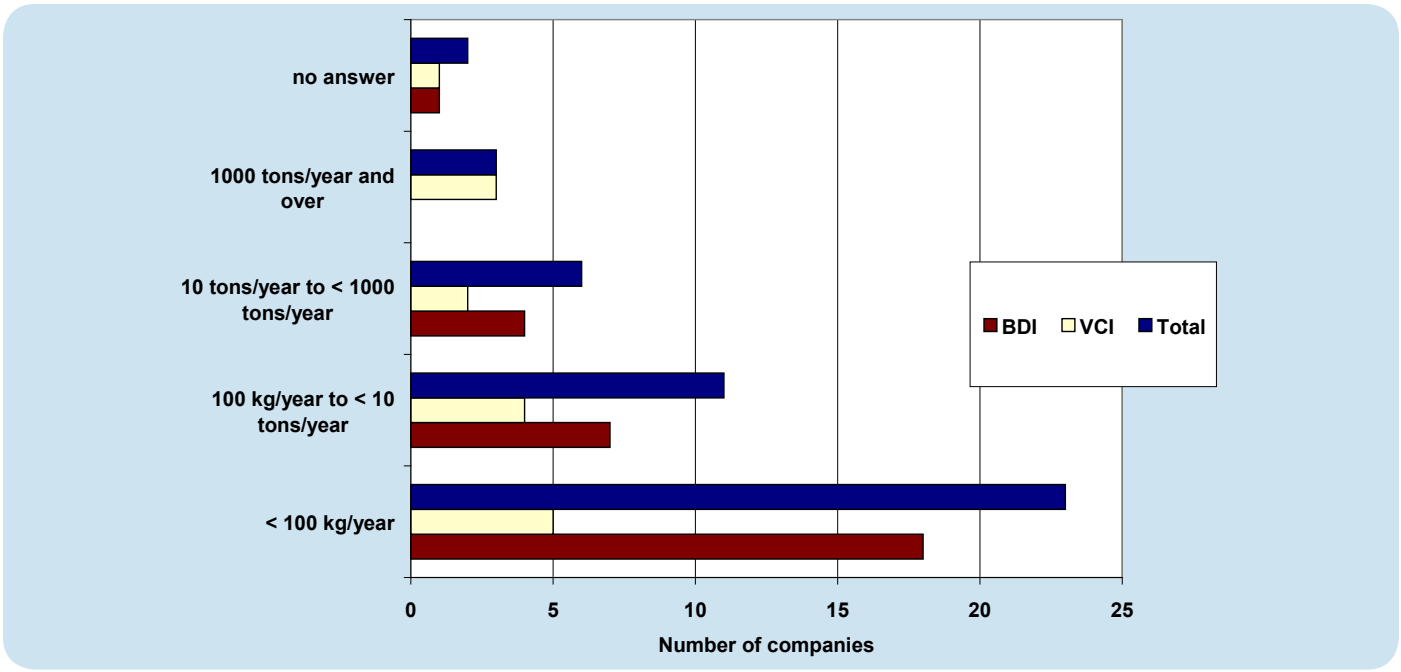

Fig. 2 Levels of activities involving nanomaterials (n=45)

[1]The questionnaire did not ask whether businesses were "young nanotechnology companies". Therefore, only an assumption can be made here.

The question regarding the number of workers who perform activities involving nanomaterials was answered by 71% of companies (n=32) with 1 to 9 workers (fig. 3). Out of these 32 companies, 75% are BDI members and probably start-up companies[1]. In only 4 companies (9%) there are over 250 workers who perform activities involving nanomaterials.

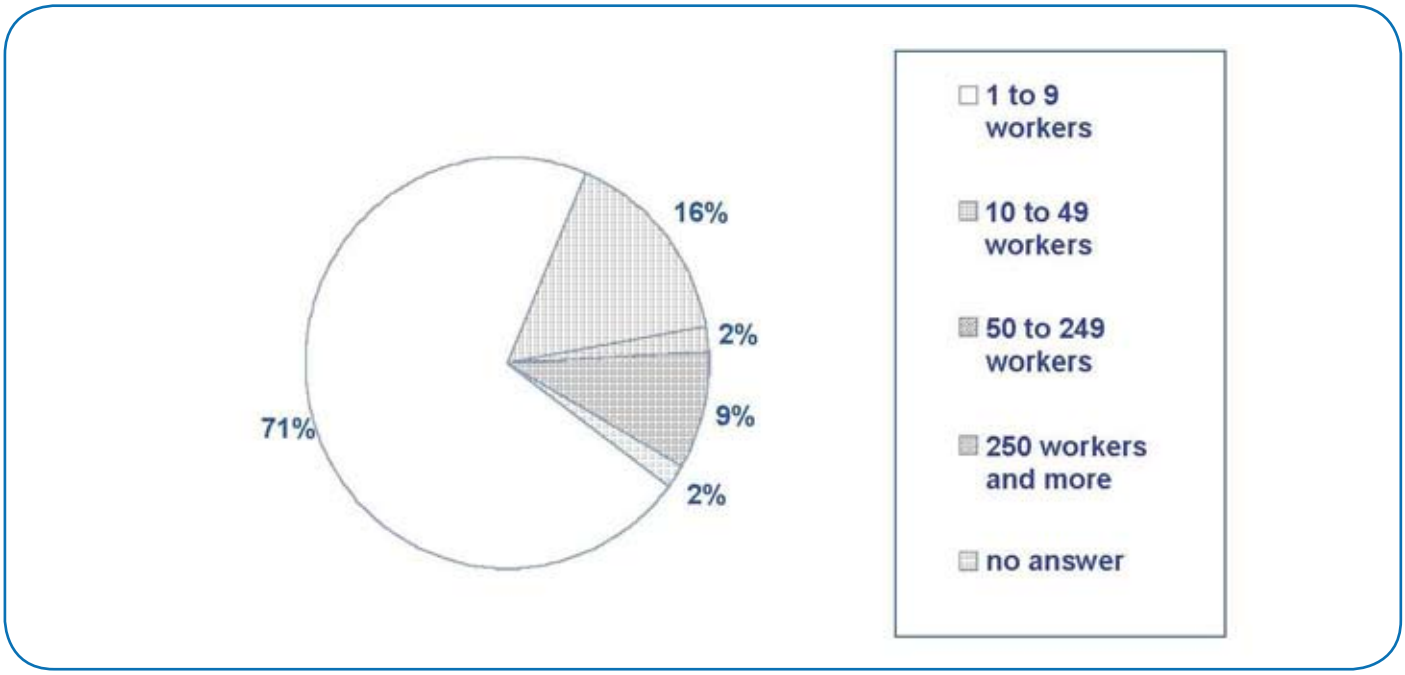

Fig. 3 Number of workers who perform activities involving nanomaterials (n=45)

Obviously the number of workers, who are engaged in the production and use of nanomaterials, is limited. Once more the large share of start-up companies is reflected. In the middle range (50 to 249 workers) only 1 company took part in the questionnaire campaign.

In the general part of the questionnaire, first data on exploratory and regular measurements of exposure were gathered. Taken into account were both gravimetric measuring of the alveolar and respirable dust fraction (standardized methods) and measuring of the particle number concentration (not yet standardized as new methods for nanoparticles).
31% (n=14) of companies carry out regular or mainly exploratory measurements at workplaces with activities involving nanomaterials. When linking the evaluation of exposure measurements for activities involving nanomaterials with tonnage, a more distinct picture is obtained (fig. 4)

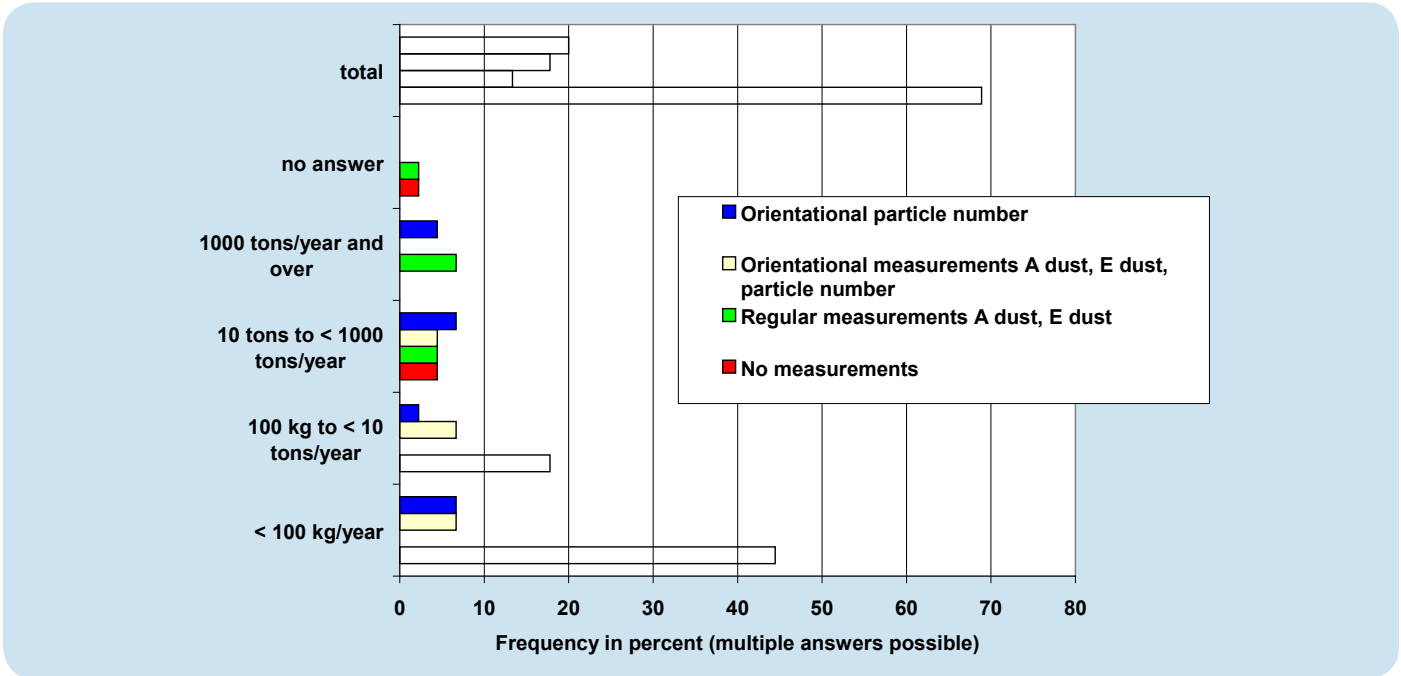

Fig. 4 Exposure measurements in activities involving nanomaterials (n=45)

Most companies who do not carry out measurements are companies who produce or handle nanomaterials in volumes of under 100 kg/year. By contrast, in larger companies (> 10 tons/year) measurements of the A and E dust fractions are carried out regularly. It is encouraging that exploratory measurements of the particle number concentration were already performed by altogether 9 companies, even though these measurements are highly work and cost-intensive. The fact that these measurements are performed for activities involving nanoparticles in small volumes (< 100 kg/year) and also by larger companies shows that both start-up companies and larger companies are aware of the sensitive nature of the nanomaterials issue. A question regarding amounts of exposure was asked in the specific part of the questionnaire.

The question whether companies had information on potential health effects of nanomaterials produced or used by the companies was answered with „yes“ by 58% (n=26). This means in particular occupational medicine data (19%), occupational medicine data and other information (15%), as well as occupational medicine and epidemiological data (16%). Furthermore it was, inter alia, pointed to biocompatibility according to German standard DIN 10993-1, in-vitro studies, clinical studies and literature research. Once more, companies without any information on health effects of produced or handled nanomaterials (40%; n=18) are mainly companies who perform activities involving nanomaterials in volumes of < 100 kg/year (n=10).
According to information from the companies, no particle-specific health complaints among their workers were known in any company at the time of our campaign.

As Federal Institute of Occupational Health and Safety (BAuA) we are particularly happy about the trust shown to us by companies, which is reflected in answering questions 5 to 8 of the questionnaire. In total, 42% (n=19) of companies are interested in support from BAuA in exploratory exposure assessments within research projects. This is an excellent opportunity for us to also invite companies, who did not take part in the questionnaire campaign, to directly contact BAuA if they are interested in exploratory exposure assessments.
As many as 47% (n=21) of companies are interested in non-compulsory advice from BAuA on occupational medicine aspects of activities involving nanomaterials.
A further question was about the passing on of information to customers on potential hazards of nanomaterials (customer information, fig. 5).

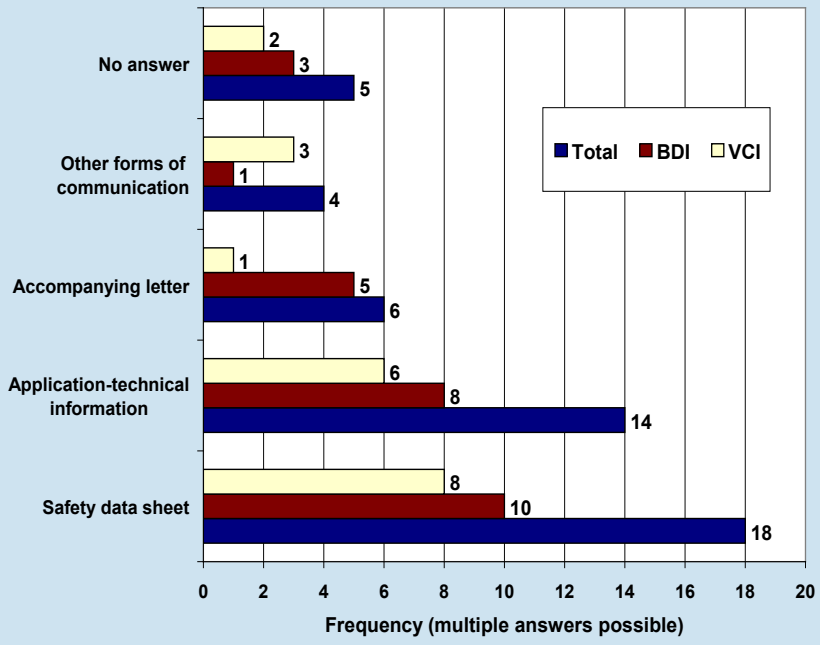

Fig. 5 Information to customers about potential hazards of nanomaterials (n=45)

25 companies (56%) pass on information on potential hazards of nanomaterials to their customers. For the other companies (44%) the question is not relevant because of the processing form of nanomaterials, or no information at all is passed on. Fig. 5 shows that information on potential health hazards is passed on mainly in safety data sheets or through other application-technical information, followed by accompanying letters or other forms of communication. No significant differences are discernible between VCI and BDI member companies, respectively.
For lower production or handling volumes (< 10 tons/year) mainly users pass on information in safety data sheets or through other application-technical information, whereas for higher production or handling volumes (> 10 tons/year) information is provided by producers and users.

2.2 Specific part of the questionnaire

The specific part of the questionnaire was designed in such a way that companies were requested to complete one separate "extra questionnaire" for each individual nanomaterial which is produced, used or handled in a company, in order to gather product-specific data. Unfortunately, there were frequently multiple answers in one questionnaire (i.e. two or more products were entered in one and the same "extra questionnaire"). Replies to queries from VCI showed that several nanomaterials are dealt with in parallel, in terms of time and work area, in some companies. For this reason, the companies saw no point in a breakdown of information. Consequently, certain data from the specific part of the questionnaire can be evaluated only with limitations, especially as the course of action taken by some companies makes a substance-specific evaluation more difficult and does not enable any conclusions regarding produced/handled volumes per individual substance.

20 companies produce, use or process only 1 nanomaterial each; further 10 companies produce, use or process 2 nanomaterials each. This means that 70% of companies handle 2 products at most. In companies handling only 1 nanoproduct, the most frequently produced, used or processed products are silicic acids and titanium dioxide, followed by iron oxide, other metal powders, silicates and pharmaceutical active substances (fig. 6). Unfortunately, no such conclusions were possible for companies handling several products.

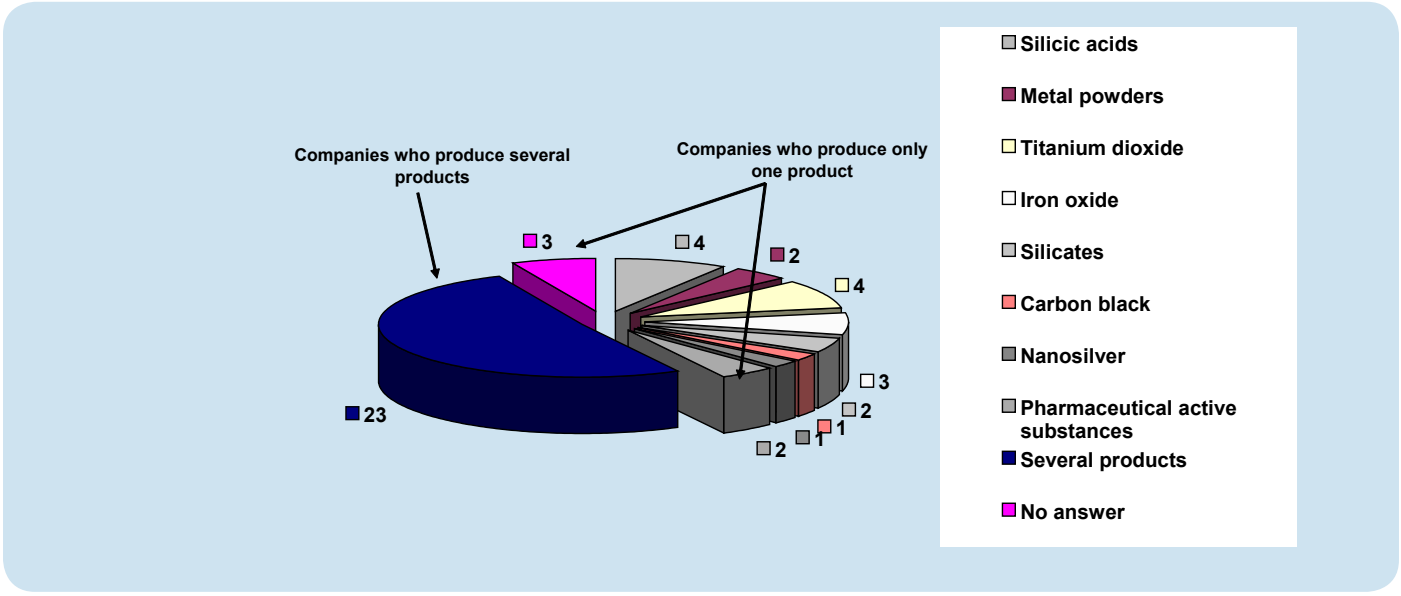

Fig. 6 Number of companies who produce, use or process nanomaterials (n=43)

As some companies produce several products, the products (n=70) – and not the companies (n=45) – are taken as basic total in this and the following evaluations.
For 85% of products (n=60) the primary particle sizes of nanomaterials are known. When stating maximum primary particle sizes (D50) of nanomaterials, the range of 20 to 50 nm was mentioned most frequently.

Evaluating activities in the handling of nanomaterials turned out very difficult, because a free text field was provided in the questionnaire for this purpose. When listing and comparing activities, it was found that mixing and dispersing were performed most frequently (n=37), followed by filling and bagging (n=31) and loading and decanting (n=17). Here, it must be observed that multiple answers were, of course, possible – i.e. activities are performed in parallel.

Questions regarding exposure at the workplace were evaluated in a product-related approach, too. Fig. 7 shows that exposures (A and E dust[2]) are not known at 72% of workplaces. It can be assumed that most activities are carried out with laboratory ventilation and involving small quantities of nanomaterials, so that gravimetric measuring – especially for substances without threshold values (e.g. TiO2) – is not performed. By contrast, E dust concentration and A and E dust concentrations, respectively, are known at 17% of workplaces.

[2] A – dust: respirable dust / E – dust: inhalable dust

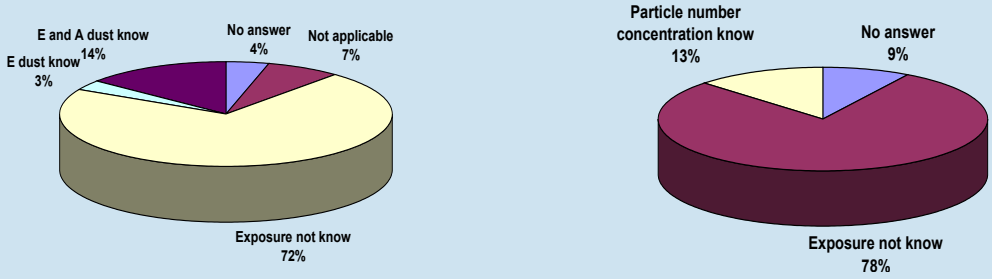

Fig. 7 Exposure measuring at the workplace (product-related, n=70)

Regarding particle number concentrations, the situation is similar. Particle number concentrations of nanoparticles are known at 13% of workplaces, while exposures are not known at 78% of workplaces. Particle size distribution is known at only 16% of workplaces with activities involving nanomaterials (78% unknown and 6% no answer).
Especially here BAuA sees considerable need for action, because – due to the complexness of the matter and already in the near future – in particular SMEs will be unable to perform, without external help, exploratory exposure measurements at workplaces involving nanomaterials.

The following table lists exposures at workplaces in activities involving nanomaterials. Here, it must be pointed to the small number of measured data and to the fact that standardized measuring methods and measuring strategies are partly not available as yet.

In view of the small number of measured data and the following observations, it is still too early to give general assessments of amounts of exposure in activities involving nanomaterials.

When taken separately from substance-specific threshold values and the nanoscale component, data from gravimetric measuring indicate compliance with general dust limit values. By contrast, particle number concentrations require commenting here, because there are no relevant threshold values for workplace or environment as yet. As mentioned earlier, existing measuring systems and measuring strategies for the particle number concentration of nanoparticles are not yet standardized, i.e. measuring systems are used that meet the state-of-the-art but remain to be validated through test standards. The need to develop generally applicable measuring strategies is made evident by the results of first measurements at relevant workplaces: It is not enough to determine the particle number in the work area. Additionally, outside air concentrations (nanoparticles are ubiquitous) need to be included, and further particle emitters (welding, separating cutting, diesel vehicles etc) in the direct surroundings of the workplace need to be quantified, in order to obtain representative measured data [3; 4; 5].

These items of background information must be considered when assessing the particle number concentrations in table 1. As the questionnaire asked, in an undifferentiated manner, about particle number concentration in the work area (irrespective of the measuring system), it can be assumed that stated data refer not only to product particles but include outside air and background emitters.

The maximum values in particle size distribution – here, too, multiple answers were possible – are between 200 and 500 nm and between 1000 and 5000 nm, respectively. Due to the small number of data, these results do not enable any general conclusions regarding the agglomeration behavior of nanoparticles.

The questionnaire campaign ended with questions about protection measures taken in activities involving nanomaterials in the companies. The question whether protection measures (product-related) are taken was answered with "yes" by 93%

	E dust concentration [mg/m³]	A dust concentration [mg/m³]	Particle number concentration [T/cm³]
Number of measured data	11	8	5
Arithmetic mean value	3.0	0.9	2.7E+05
Standard deviation	2.8	1.0	3.2E+05
Geometric mean value	2.0	0.5	1.1E+05
Minimum	0.2	0.1	0.1E+05
Maximum	10.0	3.0	6.0E+05

Table 1 Exposures at workplaces in activities involving nanomaterials

of respondents (n=65) (compared with 3% - "no"; 4% no answer). It was differentiated between process- and ventilation-technological measures and personal protective measures, respectively (fig. 8).

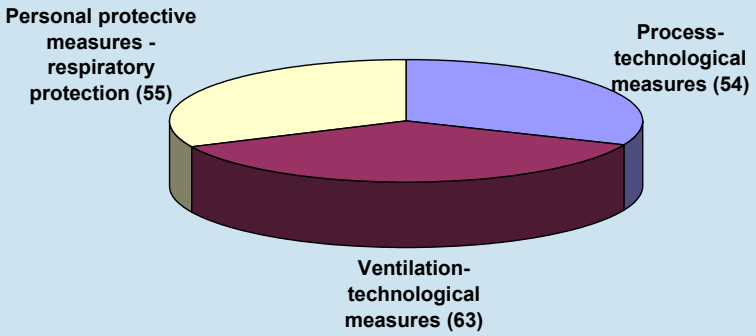

Fig. 8 Protection measures taken in activities involving nanomaterials (product-related, n=70)

Ventilation-technical measures are used most frequently. Open ventilation systems were stated most often (n=29), followed by semi-open systems (n=21) and closed systems (n=13). There was also automatic ventilation (n=18).
Where process-technological measures are concerned, wet processing ranks first (n=37), followed by closed systems (n=27) and automatic processing (n=13).
In parallel to process- and ventilation-technological measures, personal protective equipment (respiratory protection) is worn in 80% of cases, i.e. respiratory protection is used not because of lacking technical measures but mainly as an extra measure of choice. Here, a relatively wide range was stated in a free text field – from mouth protection to respiratory protection (FFP1 to P3).

3 Summary and conclusions

With a return rate of 33% the questionnaire gives a first overview of activities involving nanomaterials in Germany. This makes the questionnaire useful and informative, and it should be continued within a defined timeframe. Reasons for non answers or the partly incomplete filling out of questionnaires are not known, because questionnaires were anonymized so that no relevant queries could be addressed directly to the respondents. Here, queries over the telephone or the internet would be useful, as this is already done in other surveys. [6].

Out of 217 participating companies, activities involving nanomaterials are carried out by only 21%. The unexpectedly low number of companies, who perform activities involving nanomaterials, can be attributed to the given definition and to the starting criterion in the questionnaire. Therefore, a further developed version of the questionnaire should be brought in an even more detailed form. For example, inter alia the starting criterion for activities involving nanomaterials needs to be lowered to < 10 kg/year, and activities involving suspensions should be included, too.

The number of workers in the production and in other activities involving nanomaterials is not very high (71% - 1 to 9 workers). In particular, the middle range (50 to 249 workers) is lacking in the implemented survey. Most companies (51%) handle nanomaterials in volumes of < 100 kg/year. Only 7% of companies handle nanomaterials in volumes of over 1000 tons/year.
31% of companies carry out regular or largely exploratory exposure measurements. Most companies, who do not carry out measurements, handle nanomaterials in volumes of < 100 kg/year.
For 85% of nanomaterials, their primary particle sizes are known (maximum D50 is from 20 to < 50 nm). However, for ca. 80% of products, their particle size distributions and particle number concentrations at the workplace are not known in relevant activities – the underlying reason is a work and cost-intensive measuring technology that still needs to be validated. Here, BAuA sees considerable need for action, in order to support especially SMEs and start-ups in exploratory exposure measurements at the workplace in activities involving nanomaterials.

It is still too early to make a general assessment of amounts of exposure at workplaces with activities involving nanomaterials, based on the results of the questionnaire.
In 93% of cases (products), protection measures (process- and ventilation-technological measures and personal protective measures) are taken in activities involving nanomaterials; the questionnaire gives a first relevant overview.

By starting the questionnaire campaign, a first step was taken in Germany to gain an overview of the production, use and handling of synthetic nanomaterials. Building on these

findings, now focal areas and need for action can be identified with suitable activities to follow, inter alia in orientational measurements in SMEs and by recommending protection measures.

We thank VCI and industry delegates for their constructive cooperation.

4 Literature

[1] Guidance for handling and use of nanomaterials at the workplace
www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/Nanotechnology/Nanotechnology.html

[2] Orthen, B.: Expert survey of the research strategy on health and environmental risks of nanomaterials. August 2006.
www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/Nanotechnology/Nanotechnology.html

[3] Möhlmann, C.: Vorkommen ultrafeiner Aerosole an Arbeitsplätzen. Gefahrstoffe – Reinhaltung der Luft 65 (2005) S. 469 - 471

[4] Steinle, P.: Ultrafeine (Aerosol-)Teilchen und deren Agglomerate und Aggregate – revidierte internationale Messkonvention. Gefahrstoffe – Reinhaltung der Luft 67 (2007) S. 243 - 245

[5] Kuhlbusch, T.; Neumann, S. Fissan, H.: Number size distribution, mass concentration, and particle composition of PM 1, PM 2,5 and PM 10 in Bagging Areas of Carbon Black Production. Journal of Occupational and Environment Hygiene 1 (2004) S. 660 - 671

[6] Gerritzen, G. et al.: A Survey of Current Practices in the Nanotechnology Workplaces. February 2007.
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