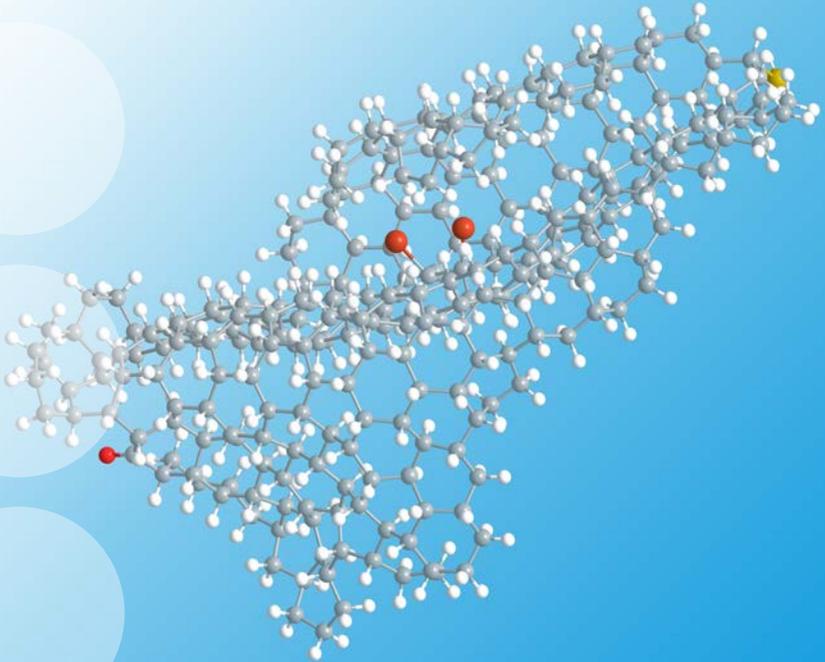


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Nanomaterials in the Laboratory

Tips and Handling Information

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Introduction

Nanotechnology is an important field for research and development, which is where nanomaterials are manufactured or processed. As defined in international standards, the key focus with nanotechnology is on the tiny structures (from approximately 1 nm to around 100 nm) in the context of the special properties caused by their tiny size (e.g. the extremely large surface area relative to the mass or also quantum mechanic effects). Nanomaterials differ from other common dangerous substances not only in terms of their chemical composition, but also because their complex spatial structure has a significantly further reaching influence. The influence of the typically very large specific surface is discussed. Highly reactive oxygen radicals may be created.

Small structures with special properties

Nanomaterials include nano-objects in the form of nanoplates and nanofilms (e.g. graphene), nanotubes and nanorods (e.g. carbon nanotubes), as well as nanoparticles (e.g. fullerene or metal oxide particles). Composite nanomaterials which either contain nanoscopic structures (e.g. embedded carbon nanotubes) or carry them on their surface (e.g. chips) are also classed as nanomaterials (Fig. 1).

Types of nanomaterials

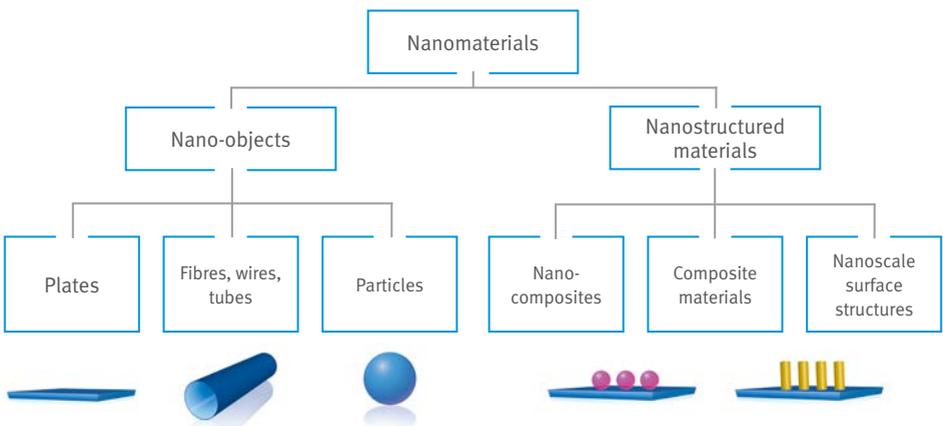


Fig. 1 Classification of nanomaterials according to ISO

Knowledge of their potential hazards remains patchy to date. For example, some toxicological investigations performed indicate that several nano-objects might have negative effects on human health, while other investigations have been unable to confirm this. The fact that several nano-objects can penetrate biological structures is already known, yet whether this can also have a negative effect remains unclear. Some fibrous nanomaterials show worrying results in animal tests.

According to a recommendation by the European Commission, all materials produced or created in processes as well as natural materials that contain unbonded nano-objects (“particles”) as agglomerates or aggregates in a numerical concentration of at least 50% (which can mean a very low weight ratio) with one or more external dimensions between 1 nm and 100 nm are to be designated as nanomaterials. Where particular concerns exist, this content level can be lowered to 1%. Fullerenes, graphene flakes and single-walled carbon nanotubes with one or more external dimensions of less than 1 nm are also classified as nanomaterials. If the particle number concentration is not known, the material is classified as a nanomaterial if it has a specific surface of at least $60 \text{ m}^2/\text{cm}^3$.

In its Announcement No. 527 on Hazardous Substances, the Committee on Hazardous Substances of the Federal Ministry of Labour and Social Affairs (AGS) proposes classifying nanomaterials into four groups according to their assumed potential impact.

- I: Soluble nanomaterials (solubility of at least 100 mg/l water under normal conditions)
- II: Biopersistent nanomaterials with specific toxicological properties
- III: Biopersistent nanomaterials without specific toxicological properties (GBP¹⁾ nanomaterials)
- IV: Biopersistent, fibrous nanomaterials

¹⁾ granular biopersistent particles

The AGS also proposes introducing concentration limits in the air at the workplace for the assessment. These limits are to be observed with the proven protective measures in laboratories under proper use.

Combustible nano-objects are potentially explosive when mixed with air. Indeed, their ignitability can be much higher than more coarse-grained materials (significantly lower minimum ignition energy than dusts). Dangerous, explosive atmospheres can be created with relatively low quantities. As little as 100 mg of fine material (or even less) can be sufficient for ignition in unfavourable circumstances. Attention must therefore also be paid to ignition sources in equipment and apparatus. Some materials (such as metals) have a tendency to spontaneously combust in fine dispersions. The reactivity can be very high and catalytic effects are also possible.

Nano-objects tend to join together to create larger units in the form of agglomerates (with weaker binding forces) or aggregates with relatively strong bonds (Fig. 2).

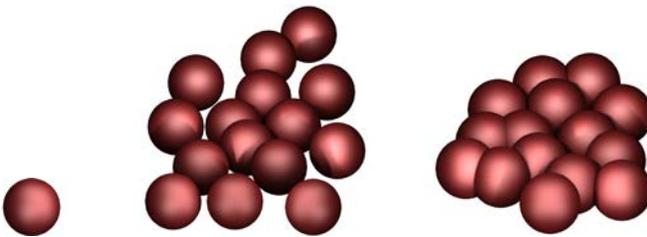


Fig. 2 Primary particle, agglomerate and aggregate (schematically)

During processing, these units can cause free nano-objects to again be released in certain circumstances, for example through grinding in a (high-performance) mill. Nano-objects can also be released in certain circumstances when processing composite nanomaterials, e.g. when removing or breaking the matrix (for example by removing

▼
Risk of fire and explosion

▼
Release from bound structures

▼
Principle of precaution

a solvent or by grinding a material with embedded nano-objects). Based on current knowledge, however, the nano-objects created in these processes seem to be formed from the destroyed material of the matrix in the systems investigated and do not appear to come from the embedded nano-objects.

A conclusive assessment of the risks cannot yet be performed based on the current level of knowledge. The principle of precaution therefore requires pragmatic solutions to be found for effective protective measures in lab work. One advantage here is that airborne nano-objects behave less like fine dusts and more like gases or vapours. This means that the standard protective measures for such material states in the lab can also be used for nanomaterials. However, free fibrous structures or those that release fibres (nanotubes, nanorods) should currently be handled with increased caution and care.

Protective measures

Exposure by inhalation

The use of standardised and tested laboratory fume hoods is an effective protective measure here. With extremely dangerous nanomaterials (e.g. those created from highly toxic materials or which are highly spontaneously flammable), glove boxes, glove bags or sealed equipment can also be used. When working in a fume hood, it is vital that the sash be (largely) closed. Formation of dust can be prevented by using nanomaterials in a wet rather than dry form (suspensions, colloidal solutions, pastes). Integration in matrices (granules, compounds) is also helpful. However, if a situation requires dry, non-compound nanomaterials to be used, as little mechanical energy as possible should be applied, as this can often lead to agglomerates breaking up and free nano-objects thereby being released into the air. Extraction systems with excessive flow rates can cause significant units (not just nanoparticles, but also larger objects) to be carried out in the exhaust air stream. It is therefore not recommended to work near the open sliding front window in fume hoods. If the window is open, even small air movements can cause particles to escape. When it is (largely) closed, this leads to high air intake speeds near the gap on the sliding front window, which can cause particles to be transported. Investigations into fume hoods in the US have shown a kind of outbreak behaviour of nano-objects, although results in Germany (tests on a fume hood as per DIN 12924-1 with several nanomaterials) were unable to confirm this. A large containment capacity was observed here. Fume hoods generally have a divided sash that makes it possible for the user to reach in from the side if necessary, which significantly increases the retention capacity of fume hoods compared to that of raised front sashes (Fig. 3).





Fig. 3 Fume hood with work performed through the divided sash

Large equipment

Large equipment, such as tube furnaces for manufacturing, should ideally not be operated in the fume hood, as they disturb the air flow. If such equipment is set up next to the fume hood, the reaction tube can be laid through the wall of and into the fume hood, thereby allowing extraction via the fume hood. If equipment of this nature really needs to be set up within the fume hood, it is vital that sufficient distance from the inner surfaces of the fume hood be provided to ensure that the air streams are impaired as little as possible. A distance of at least 5 cm from the working area in particular should be maintained (Fig. 5).

If large equipment has to be operated in the fume hood, inspecting the air flow with a smoke tube or smoke generator provides valuable information about possible disruptions or even emissions from the fume hood. Small handheld, battery-operated smoke generators have proven useful for these inspections (Fig. 4).

Closed systems

Where possible, nanomaterials that have a tendency to give off dust should be handled in closed systems if they cannot be handled safely in a fume hood. Working methods of this kind are similar to those commonly practised when handling air-sensitive or moisture-sensitive compounds in the lab. Powdery nanomaterials can be moved



Fig. 4 Testing the fume hood with a smoke generator

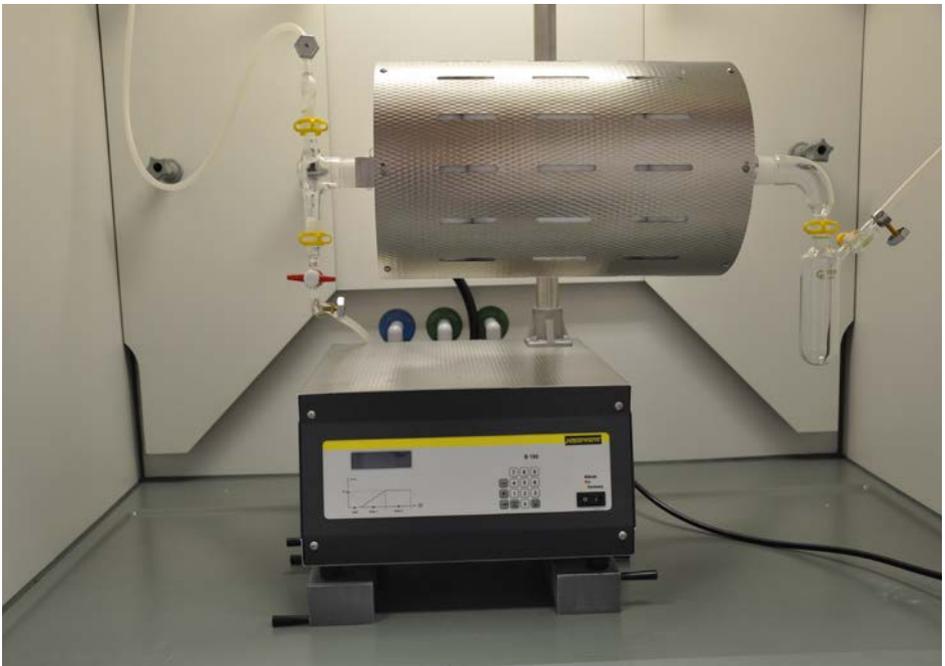


Fig. 5 Furnace placed on spacers - the apparatus is equipped with a rinsing line

Protective measures



Fig. 6 Transfer bow for powders protected from draughts (if necessary inert gas – Ar to be preferred – can be used to protect the powder against moisture and air)



Fig. 7 Transfer with a glass spatula protected from draughts (if necessary inert gas – Ar to be preferred – can be used to protect the powder against moisture and air)

from one container to another without any leakage using curved glass tubes (Fig. 6). With the help of a special Y-piece, a glass spatula can also be used for measuring out substances (Fig. 7). Apparatus can be filled, either in portions or virtually continuously, using glass vessels or – a particularly elegant solution – hand-operated (Fig. 8) or automatic (Fig. 9) powder dosing funnels. Pre and post weight measurements can be taken in the corresponding parts of the equipment in the fume hood, in the weighing chamber or in the glove box, precluding the risk of any exposure. The grinding bowls of a mill can be removed and transported in a sealed state, with the contents only being removed later in a fume hood or in the glove box (Fig. 10). Spraying of particles can be countered by preventing electrostatic charges (Fig. 11).

The powdery material can be added without the need to open the apparatus (Fig. 7, Fig. 8). The powder dosing funnel can be filled in the fume hood and also cleaned there.



Fig. 8 Manual powder dosing funnel on a three-necked flask

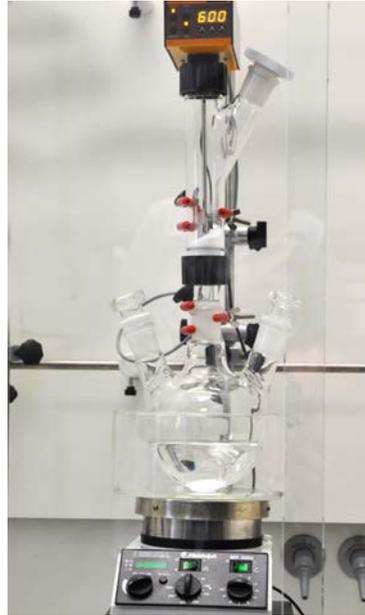


Fig. 9 Automatic powder dosing funnel on a three-necked flask for constant dosing over long periods of time



Fig. 10 Ball mill with closed grinding bowl

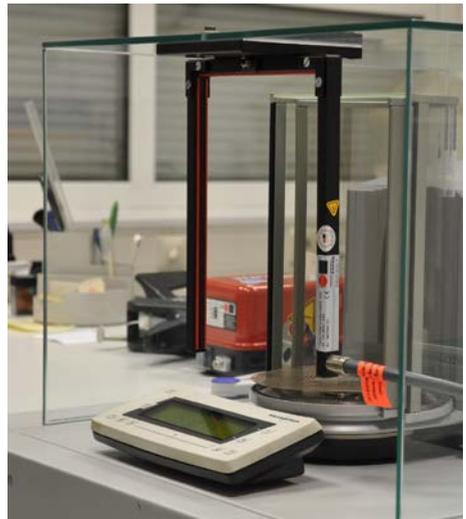


Fig. 11 Balance with electrostatic discharging equipment (U-electrode)

Protective measures

Encapsulated dosing systems (automatic scales) are very well suited for quick, low-exposure weighing (Fig. 12).

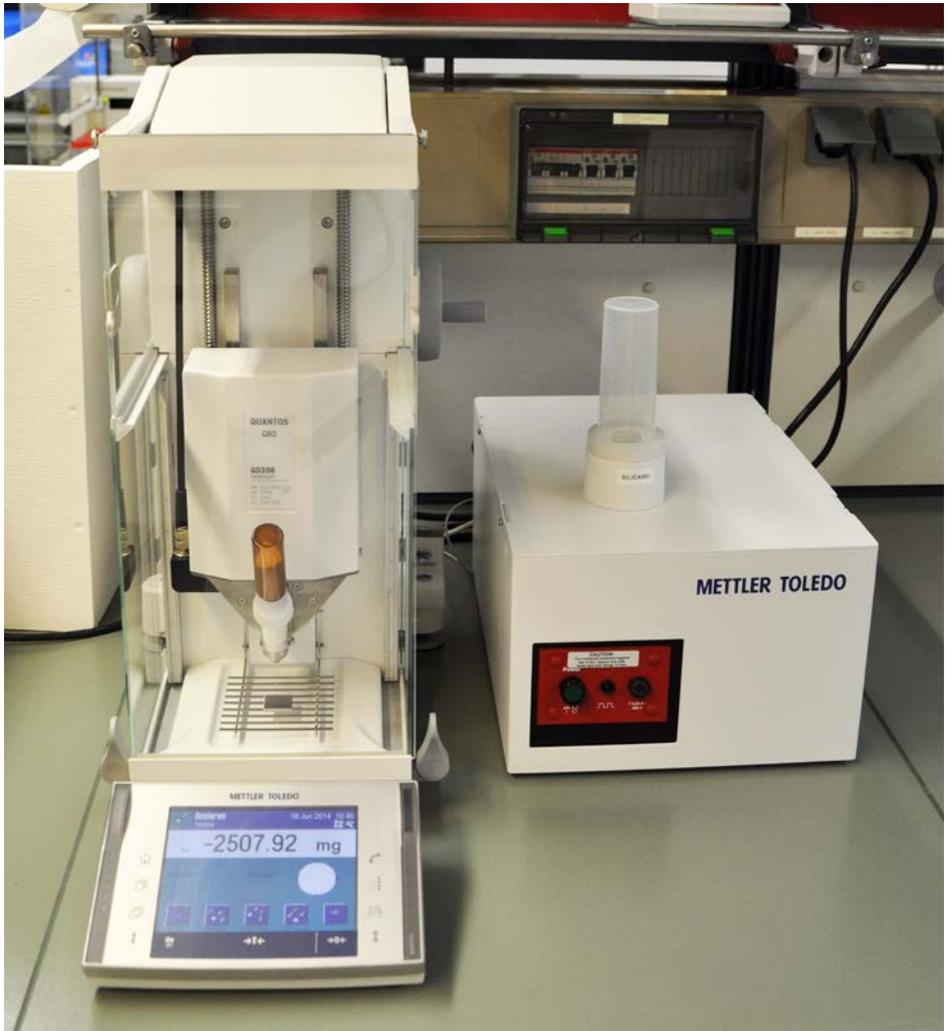


Fig. 12 Encapsulated scales with automatic dosing head



Fig. 13 Glove box with airlock



Fig. 14 Glove bag with closing clip for feed opening

A high level of protection is also achieved by working in a glove box (Fig. 13), or alternatively in a glove bag (Fig. 14), which can then be disposed of with no risk of contamination. Where necessary, the glove box also provides especially good protection against airborne influences on the nanomaterial (hydrolysis, oxidation, potential self-ignition) by providing a particularly clean inert gas atmosphere. A glove bag can also be rendered inert, however it is less impermeable to air.



Cleaning equipment

If the apparatus needs to be dismantled, for example for cleaning, it should be well rinsed before any of its contents can escape into the air in the lab. This is easy to arrange if corresponding (lockable) connections were included for rinsing lines when the system was conceived and set up (Fig. 5). Alongside any necessary connections for inert gases, these can be connections for the supply and draining of cleaning fluid, although water is generally enough here. The drained liquid can then be collected as waste in a dedicated container. When setting up the apparatus, it is important to ensure that the rinsing fluid can reach all parts of the system in which nanomaterials may be located. To prevent a pressure build-up due to evaporation of the rinsing fluid and also stress fractures, the equipment should not be rinsed at elevated temperatures. The risk of dangerous reactions between the contents of the equipment and the rinsing fluid must also be eliminated. As such, it will not be possible to use water in all cases.



Ventilation issues

If devices are to be connected to an extraction system to reduce the risk of exposure, this can also take the form of an enclosure or extraction at the source of the emissions. Here, it is vital to ensure that extraction is as complete as possible, that the speeds of the air stream in the area of the extraction system are not high enough to cause vortices to form and also that fractions of nanomaterials that move easily are carried along by the air stream. Expert design of the extraction apertures is necessary. Simply positioning an exhaust hose near the point of emission will generally be of little use or even have a potentially negative effect. For these two reasons, even in

laboratory fume hoods the air intake volume flow should not be set too high. The values set for the exhaust air volume flow (as a result of the type approval test) should also not be increased at random for „apparent safety reasons“. Nano-objects carried in the air stream can be deposited in the exhaust air systems (largely behind the extraction system's deflection wall or in exhaust channels, particularly in corners and bends). When performing maintenance work, appropriate consideration must be given to the health and protection of all persons working on the system, as well as to potential contamination of the area.

Because of the airflows that are constantly present in fume hoods, deposited nanomaterials can permanently release free nano-objects even if they are not currently being handled. Contamination on tables near airflows can also exhibit such an effect and release nano-objects into the laboratory atmosphere. The accumulation of dust should therefore be avoided.

If nano-objects genuinely need to be released in a room, respiratory protection must be worn. Class P2 or P3 particle filters are effective here. When releasing such particles into the air, appropriate consideration must of course also be given to contamination of the room.

If nanomaterials in solution or suspension are spilled they have to be removed before they get dry and possibly airborne.

It is difficult to assess the toxicity of nanomaterials in group IV. Unless it has been proven that the fibres of such a nanomaterial do not meet the WHO fibre criterion, asbestos-like effects cannot be ruled out. Appropriate minimisation through protective measures and special care when working are required. It is not possible on principle to work openly with the nanomaterial in the laboratory. Contamination of the room would necessitate particularly costly cleaning measures. Such measures are to be specified in advance. Rigid fibres in particular require special attention. Materials in group II also require careful, low-exposure handling. The use of fume hoods, glove

boxes, closed apparatus or similar secure facilities is necessary. It is recommended that you inspect the airflow conditions in and, if necessary, in front of the fume hood using a smoke tube or smoke generator, as disruptive airflows in the room when the fume hood is open can cause the atmosphere inside the fume hood to escape into the laboratory room.

Nanomaterials in group I can be assumed to have little or no potential as a toxic hazard, provided that the material itself does not exhibit toxic properties. It must be kept in mind, however, that even though these nanomaterials could be handled openly because the concentration limit of the evaluation benchmark has not been reached, there remains a residual uncertainty concerning the effect of materials that have not been investigated sufficiently. The classification only concerns toxic effects. Other effects – particularly fire and explosion risks – are not considered. Even materials that are proven to be harmless to people may still contaminate the room, which can impair testing or measuring results, for example by affecting blind values.

Nanomaterials in group III should be handled in such a way as to keep the risk of exposure to a minimum. Announcement 527 on Hazardous Substances recommends using half the occupational exposure limit (relative to the currently applicable legal workplace limit for the alveolar dust fraction according to Technical Rule for Hazardous Substances 900) as an evaluation benchmark. The evaluation benchmark should not exceed 0.5 mg/m^3 (at a concentration of 2.5 g/cm^3).

Dermal and oral exposure

Gloves should always remain in the fume hood (or any other potentially contaminated work areas). Contamination on the sleeves of lab coats can be avoided by using cuffs that can be pulled over the sleeves. These should then also be left in the fume hood. Alongside



protection from exposure by inhalation, protection from dermal and oral exposure is also necessary. Gloves should not have any openings (due to poor quality, ageing or damage). If solvents are used in production or use of nanomaterials (e. g. in suspension) the protective gloves must be qualified to withstand the solvents.

Airborne nano-objects are not only inhaled, but can also deposit themselves slowly onto surfaces. This also applies to the agglomerates and aggregates which nano-objects form at varying rates with one another or with larger particles suspended in the air. From the skin on the face, these can then find their way into the digestive tract via the mouth. This can be caused by a lack of proper hygiene practice (e. g. scratching the forehead with contaminated gloves).

Checking the effectiveness of the measures

Measurements can be helpful in assessing the situation, although issues such as the often high biogenic and anthropogenic background pollution with nano-objects and the lack of a quantitative judgement basis make this difficult. When working in the lab, however, taking measurements while performing tasks can provide useful statements regarding exposure. Portable or hand-held devices are available for this. Swipe samples or measurements with dust collectors, on the other hand, provide only limited useful information on nanoparticle exposure. There is a widely agreed upon graded measurement strategy available for any measurements that need to be carried out, which reduces what can be a considerable amount of work to a degree appropriate to the relevant exposure.



Oral intake



Measurements

Summary and Outlook



Status of current protective measures

Overall, no radically new protective measures are really necessary from today's perspective. The key here is rather to ensure consistent application of existing measures that allow dangerous substances to be monitored and controlled in the lab. The Guidelines for Laboratories (DGUV Information 213-851 „Working Safely in Laboratories“) offer the necessary information on this. The risk assessment is used to determine whether additional measures might be necessary. However, future generations of further developed nanomaterials with new properties may well lead to stricter protective measures becoming necessary.

As more knowledge is gained, it is important to keep a close eye on findings to allow swift amendments to the level of protection as and when necessary.

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Rules, regulations and information documents relating to health and safety at work

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