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Bundesanstalt für Arbeitsschutz
und Arbeitsmedizin

VCI

Guidance for Handling and Use of Nanomaterials at the Workplace

Status: 27.08.2007

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Foreword

In spring 2006 the Federal Institute for Occupational Safety and Health (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin/BAuA) and the German Chemical Industry Association (Verband der Chemischen Industrie/VCI) conducted, among VCI member companies, a joint survey on occupational health and safety in the handling and use of nanomaterials. The purpose of the survey was to obtain an overview of occupational health and safety methods currently applied in the chemical industry in activities involving nanomaterials. A further aim was to develop, on the basis of the survey results, this "Guidance for Handling and Use of Nanomaterials at the Workplace" – with recommendations and operating instructions for the handling and use of nanomaterials in the chemical industry.

The starting point for both joint initiatives of BAuA and VCI was the stakeholder dialogue event on "Synthetic Nanoparticles" on 11./12. October 2005 in Bonn.

The questionnaire survey was evaluated by BAuA; the "Guidance for Handling and Use of Nanomaterials at the Workplace" was elaborated predominantly by VCI. In both activities several expert talks were held between BAuA and VCI in the development phases.

This Guidance wants to provide some orientation regarding measures in the production and use of nanomaterials at the workplace. The recommendations given here reflect the current state of science and technology.

It is planned to adapt this Guidance to the advancing state of knowledge and to bring it in a more specific form, by mid-2008 at the latest.

Berlin/Dortmund/Frankfurt, August 2007

Guidance for Handling and Use of Nanomaterials at the Workplace

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I. Introduction

I.1 Background

In spring 2006 the Federal Institute for Occupational Safety and Health (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin/BAuA) and the German Chemical Industry Association (Verband der Chemischen Industrie/VCI) conducted, among VCI member companies, a joint survey on occupational health and safety in the handling and use of nanomaterials. The purpose of the survey was to obtain an overview of occupational health and safety methods currently applied in the chemical industry in activities involving nanomaterials. A further aim was to develop, on the basis of the survey results, this "Guidance for Handling and Use of Nanomaterials at the Workplace" – with recommendations and operating instructions for the handling and use of nanomaterials in the chemical industry.

The survey was initially addressed to industrial manufacturers and users of nano-materials, covering primarily products that had been manufactured and used for many years. Products still in the research phase were also included in the survey; they are taken into account in this Guidance[1].

This Guidance wants to provide some orientation regarding measures in the production and use of nanomaterials at the workplace. The recommendations given here reflect the current state of science and technology.

According to the draft by the ISO Technical Committee 229 "Nanotechnologies" – which was taken over as working definition by OECD – *nanomaterials* are understood to be either so-called *nano-objects* or *nanostructured materials*. *Nano-objects* are materials which are confined in one, two, or three dimensions at the nanoscale *(approximately 1 – 100 nm)*; typical examples are nanoplates, nanorods and nano-particles. Nanoparticles are nanoobjects with three dimensions at the nanoscale.

[1] Also start-up companies (list of the federal ministry of education and research/BMBF) took part in the survey. In this way, also companies were included that handle nanomaterials within research activities (in volumes > 10 kg/year).

Nanostructured materials have an internal structure *at the nanoscale*. Typical examples are *aggregates* and *agglomerates* of nano-objects.

Usually highly sophisticated chemical and physical processes are needed to manufacture nanomaterials as nanoparticles in isolated form. However, in most products currently manufactured commercially in larger volumes, nanoparticles do not come as individual particles but as aggregates and agglomerates of various particles.

Aggregates and agglomerates are not nanoparticles in the meaning of this definition (see above); they are nanostructured materials whose nanoparticles are linked with each other. Without major energy input a release of nanoparticles from these aggregates and agglomerates is often not possible.

In some instances, nanoparticles are processed into granules, formulations, dispersions or composites already by their manufacturers. In many cases a release of isolated nanoparticles in subsequent uses is largely no longer to be expected.

I.2 Production processes

The chemical industry produces nanomaterials mainly in two processes: By synthesis in the gaseous phase, i.e. through reaction in a flame, or by reaction in solution. In the gaseous phase reaction, individually produced primary particles very rapidly link to form larger units. Isolated nanoparticles can be produced through reaction in solution, by adding stabilizing agents and depending on the solution medium. Such isolated nanoparticles are either further processed as dispersions, or they are obtained by evaporating the solvent and then further processed.

If only for technical reasons, gaseous phase synthesis of nanomaterials takes place predominantly in closed systems. As an extra measure, these systems are often run at under pressure. Workers' exposure in production is possible mainly at interfaces - such as filling, sampling, cleaning and maintenance work - or in disruptions of normal operations, which call for a particularly high degree of attention where safety technology is concerned.

In activities in liquid media (e.g. precipitation reactions, dispersion in the liquid phase), intake by inhalation is usually excluded by avoiding aerosol formation.

II. General occupational health and safety rules

Like for all other chemical substances, activities involving nanomaterials are subject to occupational health and safety rules and to the provisions of the German Dangerous Substances Ordinance (Gefahrstoffverordnung), with the legal basis being formed by relevant EC Directives. By assessing possible hazards to workers that might be connected with their activities, employers must identify occupational health and safety measures to be taken. These include design and structure of the workplace in its entirety and of individual workstations, as well as measures to reduce exposure to physical, chemical and biological impacts. Furthermore, technical rules for hazardous substances laid down at a subordinate legal level (e.g. TRGS 500, TRGS 401) must be observed (TRGS = Technische Regeln für Gefahrstoffe/technical rules for hazardous substances).

For many insoluble nanomaterials it cannot be excluded at present that an intake by inhalation of these very small particles might pose hazards at the workplace – irrespective of the classification of these substances based on their chemical composition.

The following course of action to protect workers from hazards is laid down in the Dangerous Substances Ordinance: 1. Information gathering, 2. Hazard assessment, 3. Determination of protection measures, 4. Review of effectiveness of measures, 5. Documentation. To be taken into account are all work processes and operating states, including maintenance, repairs, disruptions/breakdowns and control activities.

II. 1 Information gathering

Information gathering includes:

- Information on the product used (properties, volume, type and form of use)
- Information on the activity (in particular work steps that can lead to intake by inhalation or to dermal or oral intake). For oxidizable materials, also fire and explosion risks must be included.
- Information on substitution options for hazardous substances (including any use of processes or preparations of the substance that result in lower hazard).
- Also to be gathered is information on the effectiveness of protection measures already in place and, if applicable, information on implemented activities in preventive occupational medicine.
- In case of data gaps, this lack of information must be adequately taken into account when determining protection measures.

Sources of information gathering on substance properties are, inter alia, material safety data sheets, labelling information, communications from manufacturers, technical rules and rules by employers' liability insurance associations (Berufsgenossenschaften), publications by competent authorities and organisations, as well as literature data.

II.2 Hazard assessment

Hazard assessments are implemented based on information gathered. Under the German Industrial Health and Safety Act (Arbeitsschutzgesetz), a hazard assessment must take into consideration substance-related hazards and all further (e.g. mechanical or electrical) hazards.

II.3 Determination of protection measures

In order to determine technical, organisational and personal protection measures, the following points must be examined based on the hazard assessment:

1. Substitution options:

Examination whether health-endangering substances or technical processes can be replaced by less dangerous substances or processes (e.g. substance variations with reduced emissions).

2. Technical measures:

Use contained installations and capture, limit and remove dangerous gases, vapours and dusts, at source if possible.

3. Organisational measures:

Adequate washing facilities, protected storage of clothing not worn for work purposes, further hygiene measures, time arrangement of operational sequences, training and instruction, access and storage rules etc.

4. Personal protection measures:

Use of personal protective equipment, additionally to technical and organisational measures.

II.4 Review of effectiveness of measures in place

Like for all other working materials, the effectiveness of measures in place must be reviewed regularly for nanomaterials, too. Also in cases where no health-based limit values have been laid down so far, the exposure of workers should be determined after relevant measures were introduced according to good working practice. The following statements in this Guidance are intended to provide assistance in this respect, also pointing to possibly suitable measuring methods.

II.5 Documentation

The documentation of hazard assessments is a binding requirement pursuant to the Dangerous Substances Ordinance. Especially in connection with nanomaterials, for which no health-based limit values can be established as yet, it is particularly important to document protection measures taken, substances used, working conditions and possibly available measurement data on strains – for assessment at a later stage.

III. Recommendations for workers' protection in the handling and use of nanomaterials

Protection measures necessary at the workplace are determined based on hazard assessments. Existing threshold values – e.g. general dust limit values for the alveolar and respirable dust fraction or substance-specific limit values – must be observed. According to the current state of knowledge it cannot be ruled out that exposure to nanomaterials might have specific effects, different to the effects of larger particles in the micrometre range. Pursuant to TRGS 900 general dust limit values do not apply in the assessment of ultra-fine dusts (this is understood to mean a dust fraction with a particle size of under 0.1 µm diffusion equivalent diameter, including its agglomerates and aggregates). Up until specific limit values are laid down for nanoparticles or certain nanomaterials it should, therefore, be striven to minimise exposure. Recommendations of TRGS 401 must be observed regarding dermal exposure.

The following course of action is recommended to determine protection measures:

1. Substitution options:

Bind powder nanomaterials in liquid or solid media. Use dispersions, pastes or compounds instead of powder substances, wherever this is technically feasible and economically acceptable.

2. Technical protection measures:

Perform activities in contained installations, wherever this is possible.

If this cannot be done, avoid the formation of dusts or aerosols. To this end, extract possibly forming dusts or aerosols directly at their source (e.g. in filling and emptying processes), depending on the materials produced and production conditions. Ensure regular maintenance and function testing of extraction facilities.

Extracted air must not be recirculated without exhaust air purification.

3. Organisational protection measures:

Instruct the workers involved, in a targeted manner, about the specific physical properties of free nanoparticles, the need for special measures, and potential long-term effects of dusts. Include relevant information in the operating instructions.

Keep the number of potentially exposed workers as small as possible..

Furthermore, deny unauthorised persons access to the relevant work areas.

Ensure clean work wear. Work wear must be cleaned by the employer. Work wear and private clothing must be stored separately. Ensure the regular cleaning of workplaces. The only way to remove deposits or spilled substances is with a suction device or to wipe them up with a moist cloth; do not remove them by blowing.

4. Personal protection measures:

Where technical protection measures are not sufficient or cannot be put into place, personal protection measures – such a respiratory protection (e.g. filters of protection levels P2, FFP2, P3 or FFP3, to be selected in the hazard assessment) – are a suitable step. Depending on substance properties, it might be necessary to wear protective gloves, protection goggles with side protection and protective clothing. Where respiratory protection equipment is used, limited wearing times and preventive occupational medical checks must be observed.

With particles in the size range between 2-200 nm the efficacy of filters increases with decreasing particle size. This is because below 200 nm the diffusion of particles gets much stronger; when flowing through the filter medium, the particles are thus more likely to collide with the fibres of the filter medium where they are bound. Measuring data from the Berufsgenossenschaftliches Institut für Arbeitsschutz (BGIA)* substantiate a "total number penetration efficiency" for three P3 filters - used for sodium chloride particles from 14 and 100 nm - of between 0.011 and 0.026%, referred to the particle count. Data for P2 filters show a penetration of 0.2%, referred to the particle count.

* The BGIA is an institute for research and testing of the German Berufsgenossenschaften (BG), the institutions for statutory accident insurance and prevention in Germany.

In the selection of protective gloves, it must be ensured that the glove material is suitable. The glove material must fulfil requirements for maximum wearing time under practical conditions. An important relevant criterion is the permeation time (break-through time depending on glove material and material strength). Additionally to hand protection, it can be necessary to protect further parts of the skin with protective equipment. This includes in particular protective suits, aprons and boots.

Additionally to the dust protection measures mentioned here, it is also necessary to observe further measures ensuing from special substance properties - e.g. extra anti-explosion measures in the handling of oxidizable nanomaterials, or specific protection measures in the handling of reactive or catalytic nanomaterials. Besides measures designed specifically for nanomaterials, all measures resulting from the hazard assessment must be complied with, too, so that inter alia the occupational exposure levels at the workplace for further working substances - e.g. for solvents – are observed.

The effectiveness of applied protection measures (e.g. personal protective equipment) must be reviewed.

5. Flowchart "Hazard Assessment for Nanomaterials at the Workplace (by inhalation)"

The scope of this flowchart covers targeted activities involving nanomaterials (see attached flowchart).

IV. Current situation and development of measuring methods for nanoparticles

At present, it is not yet possible to definitely state how nanoparticles should best be characterized for their HSE effects. Studies point to specific surface and particle number concentrations as well as structure and composition of nanoparticles for dose measurment. In this context, particle mass seems to be of less importance. Thus standard gravimetric measuring methods can be used only as accompanying steps when determining exposure to nanoparticles.

In measurement of nanoparticles, stationary equipment is used to determine particle number concentration and surface concentration of nanoparticle emissions in air at the workplace. This is an expensive and work-intensive measuring method which meets the state-of-the-art, but it is not yet standardized or validated. [2].

In measuring activities, particles manufactured industrially and intentionally cannot be differentiated from nanoparticles from other sources (background exposure at the place of production). Such influences must be taken into account in evaluations of measurements of nanoparticles (e.g. ca. 1 million particles/cm^3 in a smoker room or 100,000 particles/cm^3 at roads with heavy traffic).

IV.1 Measuring methods

The following measuring methods are currently available[3]:

- The Condensation Particle Counter (CPC) is the most wide-spread method for measurements of particle number concentration in the nanometre range. CPC enables particle counts in the nanometre range and above, with detection by light dispersion, but CPC does not obtain data on particle size and chemical composition of particles[4]. Quite often, CPC is used in combination with a size classifying instruments such as a Scanning Mobility Particle Sizer (SMPS) e.g. The Scanning or Stepped Mobility Particle Sizer (SMPS) is the most frequently used instrument for measuring particle size distribution in the size range from 3 to 800 nm. The SMPS method determines the mobility or diffusion equivalent diameter, respectively. Modifications of this method enable a wider range of measurable sizes. However, possibilities to use this method are limited due to its complex nature.

- Aerosol mass spectroscopy is a wide-spread method for the chemical on-line analysis of particles and aggregates in the size range of over 100 nm. Electron microscopy (TEM/SEM) is the available off-line method to find out about size,

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[2] The suitability of measuring methods and protection methods is assessed by the federation of institutions for statutory accident insurance and prevention (Hauptverband der gewerblichen Berufsgenossenschaften – HVBG). Further information on suitable measuring methods is given e.g. in the BGIA work folder "Measuring of dangerous substances" (Arbeitsmappe: Messung von Gefahrstoffen). The websites of HVBG and employers' liability insurance associations contain more details on the suitability of respiratory protection filters.

[3] This description of measuring methods includes commonly used methods, with no claim to completeness.

[4] In measuring technology the term particle is used not only for single particles but also for agglomerates and aggregates.

morphology and particle structure. But here, too, wider use in routine measuring is hampered by complex technical aspects. Energy Dispersive X-Ray Fluorescence Analysis – in combination with electron microscopy – enables a substance determination of particles, with resolution of spatial element distribution. So far, this method allows up to now only semi-quantitative analysis.

- Besides SMPS, the Nano-Aerosol Sampler (NAS) is a further option for separating particles in the size range from 1 to 1000 nm, e.g. on a TEM grid, for subsequent characterisation with TEM/EDX regarding morphology and element composition. However, up until now only a semi-quantitative evaluation is possible.

IV.2 Use of measuring methods in operational practice

Up until now, particle strains are assessed based on mass concentration. However, the measuring of nanoparticles based on mass is only of limited informative value: The total mass of nanoparticles remains comparative low at high particle concentrations. In particular, it must be emphasised that individual measuring results for nanoparticles in air cannot really be compared with each other, because at present the exposure measuring methods are not fully standardized as yet.

A standardized – and thus generally accepted – method is the monitoring of work areas by measurement of dustiness (respirable fraction) [5]. In the scientific discussion this method is deemed insufficient. There is a need to develop standardized and, most importantly, personal measuring methods for particle counts and sizes. In future, measuring with the "Scanning Mobility Particle Sizer" technique for particle count and particle size distribution could provide further information on exposure in work areas.

IV.3 Standardization of measuring methods

The standardization of general conditions for measuring methods relevant in occupational health and safety (i.a. sampling, sample treatment, monitoring methods in occupational health and safety, reference materials) is currently driven forward by the International Organization for Standardization (ISO) and the German standardization institute DIN.

IV.4 Safety research regarding measuring methods

"NanoCare" is a cooperation project of chemical industry companies and university research institutes, promoted by the German federal ministry of education and research (BMBF). The project examines, inter alia, agglomeration and aggregation behaviour as well as the stability of agglomerates and aggregates of primary particles at the nanoscale. Furthermore, NanoCare compares existing measuring methods for

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[5] According to BGIA work folder – Arbeitsmappe, method 7284, and fine dust measuring (alveolar dust fraction) according to BGIA – method 606.

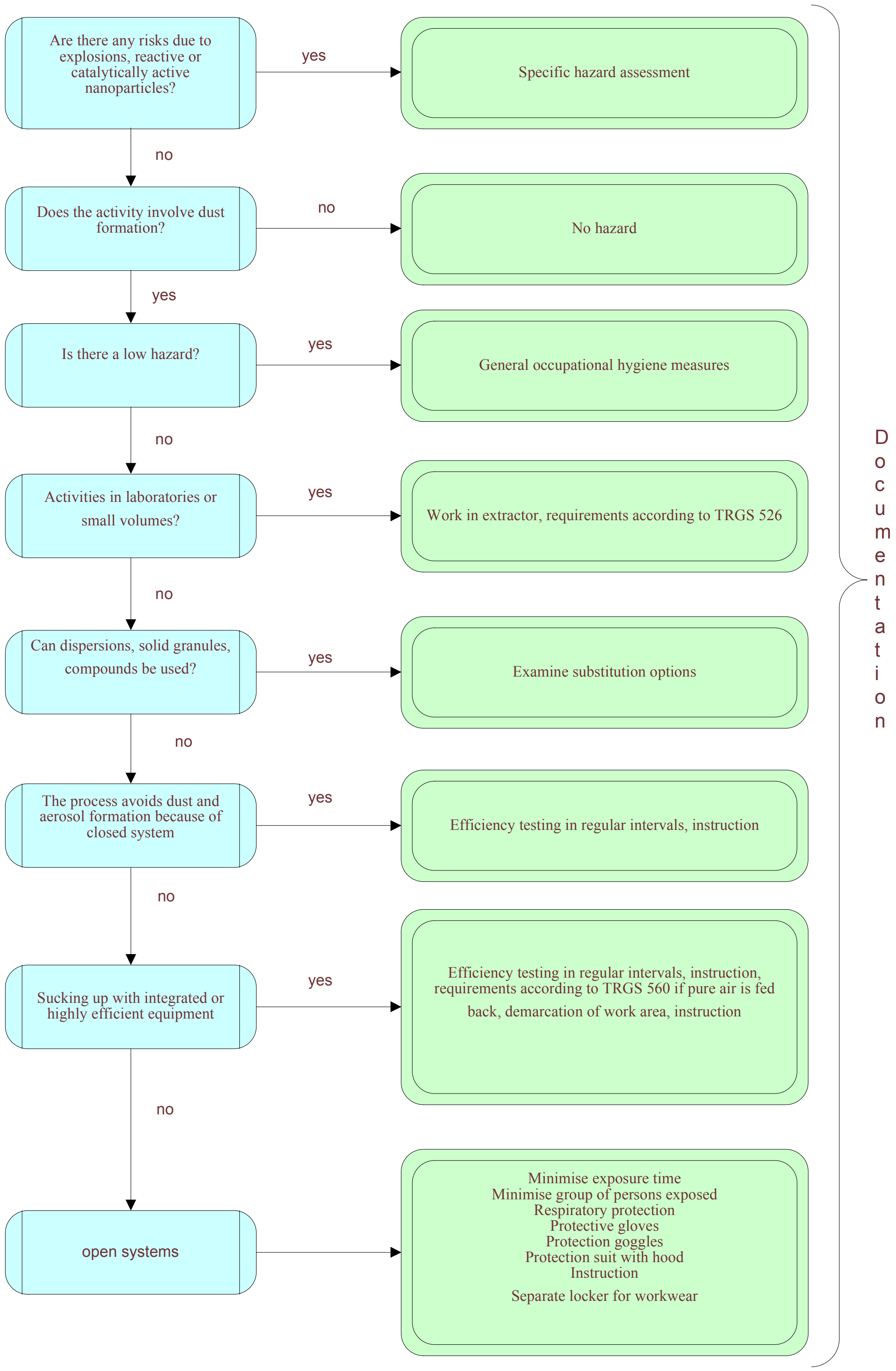
the determination of airborne particles and aerosols, using materials that are modified and adjusted in a targeted manner to be taken as reference materials in this project. Another NanoCare activity is the further development of measuring methods for parameters of dustiness (Staubungskennzahlen). [6]

The chemical industry has a decisive role in further projects, such as e.g. "Nanosafe II", "Nanoderm", "Tracer" and also implements own research projects. All ongoing research projects were already specified in the "Roadmap for Safety Research on Nanomaterials" of the DECHEMA/VCI working group "Responsible Production and Use of Nanomaterials".

In November 2006 BAuA (federal institute for occupational safety and health), UBA (federal environment agency) and BfR (federal institute for risk assessment) and the ministries BMAS (labour and social affairs), BMU (environment, nature conservation and nuclear safety) and BMELV (food, agriculture and consumer protection) discussed their draft for a research strategy regarding potential risks of nanotechnology with delegates from science, research and industry, taking first steps toward its implementation.

[6] Measuring of the tendency of certain substances to release dusts.

Flowchart: Hazard Assessment for Nanoparticles at the Workplace



List of abbreviations

AGW:	**Arbeitsplatzgrenzwert nach Gefahrstoffverordnung** (Workplace limit value under the German Dangerous Substances Ordinance)
BAuA:	**Bundesanstalt für Arbeitsschutz und Arbeitsmedizin** (Federal institute for occupational safety and health)
BfR:	**Bundesinstitut für Risikobewertung** (Federal Institute for risk assessment)
BGIA:	**Berufsgenossenschaftliches Institut für Arbeitsschutz** (Institute for research and testing of the German Berufsgenossenschaften/BG)
BMAS:	**Bundesministerium für Arbeit und Soziales** (Federal ministry of labour and social affairs)
BMBF:	**Bundesministerium für Bildung und Forschung** (German federal ministry of education and research)
BMELV:	**Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz** (German federal ministry of food, agriculture and consumer protection)
BMU:	**Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit** (Federal ministry for the environment, nature conservation and nuclear safety)
CPC:	**Condensation Particle Counter**
DECHEMA:	**Gesellschaft für Chemische Technik und Biotechnologie e. V.** (Society for Chemical Engineering and Biotechnology)
DIN:	**Deutsches Institut für Normung e. V.** (German standardization institute)
EDX:	**Energy Dispersive X-Ray Analysis**
HVBG:	**Hauptverband der gewerblichen Berufsgenossenschaften** (Federation of institutions for statutory accident insurance and prevention)
ISO:	**International Organization for Standardization**
NAS:	**Nano-Aerosol Sampler**
SEM:	**Scanning Electron Microscopy**
SMPS:	**Scanning *or* Stepped Mobility Particle Sizer**

TEM: **Transmission Electron Microscope**

TRGS: **Technische Regeln für Gefahrstoffe** (Technical rules for hazardous substances)

UBA: **Umweltbundesamt** (Federal environment agency)

VCI: **Verband der Chemischen Industrie e. V.**
(German chemical industry association)