DGUV
Deutsche Gesetzliche
Unfallversicherung
Spitzenverband

213-027

DGUV Information 213-027

Safety in University Chemistry Courses

An Introduction for Students

October 2009

Deutsche Gesetzliche
Unfallversicherung

Information

Safety in University Chemistry Courses

An Introduction for Students

BGI/GUV-I 8553 E October 2009

Published by:
Deutsche Gesetzliche
Unfallversicherung (DGUV)

Mittelstraße 51, 10117 Berlin
Tel.: +49 30 288763800
Fax: +49 30 288763808
E-Mail: info@dguv.de
Internet: www.dguv.de

In cooperation with the Gesellschaft Deutscher Chemiker (GDCh)
and the Berufsgenossenschaft Rohstoffe und chemische Industrie (BG RCI),
formerly BG Chemie.

This brochure is permanently being updated by the DGUV working team “Gefahrstoffe”.

Translated by the Chevalier Dr. Dr. Rüdiger Marcus Flaig

The October 2009 edition corresponds to the German version of the brochure “Sicheres Arbeiten in chemischen Laboratorien” (BGI/GUV-I 8553), October 2009.

BGI/GUV-I 8553 E can be obtained from your competent accident insurance provider. The addresses are to be found at www.dguv.de

Deutsche Gesetzliche
Unfallversicherung

Information

Safety in University Chemistry Courses

An Introduction for Students

BGI/GUV-I 8553 E October 2009

Table of Contents

1 Introduction to lab safety

Safety in the chemical lab in 1939:
About 30 of us ... had been admitted to the Laboratory for Qualitative Analysis during our second academic year. We had entered the spacious, soot-blackened, murky hall like somebody who carefully places his steps while entering a place of worship ... Nobody had bothered to waste much breath on teaching us how to protect ourselves from acids, corrosives, fires and explosions: Manners were rough at the institute, and obviously there was confidence that natural selection would do its duty and pick those among us who were best adapted to physical and professional survival. There were only few exhausters; in systematic analysis everybody meticulously released, as prescribed by the textbook, copious quantities of hydrochloric acid and ammonia so that the lab was continuously filled with a dense white fog of ammonia chloride precipitating on the window panes in the form of tiny glittering crystals. Into the room with hydrogen sulphide, where the air was murderous, there retired couples desiring to be alone or mavericks to eat their lunch.
(Primo Levi: The Periodic Table, Carl Hanser Verlag)[*]

Over the course of their training and professional work, today's chemists acquire extensive knowledge and experiences relating to the risks and dangers inherent in their work and to the products developed by themselves and their colleagues. The resulting safety awareness is an integral part of their professional ethos. The skills and knowledge acquired in the field of safety are just as important as those relating to the profound complexities of science or to cutting-edge technological developments.

---

[*] *Publisher of the German version (Das periodische System). English version with the title given here published in September 1996 by Random House, ISBN: 978-0-679-44722-1. Title of the Italian original: Il systema periodico, ISBN: 978-8806135171*

Thus it is an important goal of academic training to educate chemists to

- be proficient in safe and secure handling of chemicals and thus,
- protect both themselves and their colleagues and employees from dangers,
- act responsibly towards the environment and the general public,
- identify possible dangers in the use of chemical products by consumers and avert these dangers by providing proper instructions.

Professional knowledge is linked to the obligation not only to act as described above but also to demonstrate to the general public that safe and secure handling of chemicals is possible and actually being practised, and that application of chemical products by the consumer is guaranteed to be safe if the instructions for their use are complied with. The insurance providers' accident statistics show the success of consequent compliance with safety regulations.

Safety matters in the chemist's professional work are regulated by numerous laws, ordinances, directives and guidelines, but safety awareness based on solid professional knowledge still exceeds this by far. Thus, safety awareness can and must be learned and acquired just like any other professional knowledge. For the student in the field of chemistry, this begins with the practical courses and the very first experiments in chemistry.

Accident prevention as a self-assigned task with personal responsibility is a goal of training. It is of particular importance as the chemist will, at latest when having to issue instructions as a superior in industry or academia to subordinates, be held responsible for the safety of these persons and will have to face civil and penal consequences, should the situation arise.

A study of thousands of workplace accidents in laboratories and production plants has revealed that they were caused by technical defects only in minority of cases, but in the vast majority, that is to say, in about 85% of cases, by human errors. Ignorance of safety-relevant properties of substances or lack of insight into the type of reactions performed often plays a role in this.

However, habituation is just as inimical to consciously safe work: Persons who have, due to long-term experience, lost the initial respect for a potentially hazardous method tend to neglect safety precautions.

Here the best prevention is to consequently and regularly attend all safety briefings offered.

Some examples of laboratory accidents will illustrate the above.

Even test tube scale experiments may be dangerous

In order to produce cyclohexanone peroxide, a chemist heated a mixture of 0.5 ml of cyclohexanone and 0.5 ml of hydrogen peroxide in a test tube. A violent reaction detonated the test tube. The chemist suffered injuries of his face and both hands. The left pane of the safety goggles was shattered. The eyes remained unharmed.

It is mandatory to know substance properties

A technician was instructed to bottle silver perchlorate precipitated from solution and dried in an exsiccator. When she was crushing the substance with a spatula, it exploded with such vehemence that she died from her injuries four weeks later.

Waste disposal rules are to be observed

A student of chemistry illegally poured cyanide-containing wastes into a sink. When another student poured hydrochloric acid into the same sink shortly afterwards, hydrogen cyanide was released, inhalation of which quickly led to the second student's death.

Ignition sources, they are everywhere

In a research laboratory many preparations, some of which contained highly flammable solvents, were stored in a normal housekeeping fridge. Leakiness of one vial resulted in an explosive vapour-air mixture which was ignited by the switching spark of the thermostat of the fridge, resulting in a severe explosion followed by fire and considerable damage to property.

2 Before beginning the practical course

2.1 Where are important installations and accessories?

Please check! Can you answer all of the following questions?

Where are:


emergency exit, fire escape, general escape routes?


alarm systems, telephone, emergency call, assistant's room?

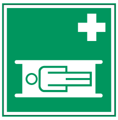

fire extinguisher, fire alarm box?


respiratory protection masks and filters?

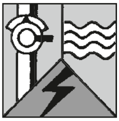

body showers, fire blankets?


eye showers?


First Aid cabinets?

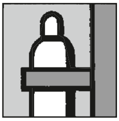

First Aid room, stretchers?

Do you know, e.g.,


how and/or by whom media (gas, water, electricity) can be switched off?


that in case of fire you must not use a elevator?


that fire extinguishers must be refilled after every use?


that pressurized gas cylinders must always be guarded against tilting?


what self-protection means?


what to do in case of severe accidents?


which of the chemicals you may have to work with are toxic, explosive or flammable?


where to find safety information?

With regard to the localities you must find out for yourself; concerning other issues this brochure is intended to help you.

2.2 How to learn about dangerous properties of substances and safety-relevant parameters

Usually, operating procedures in text books and protocols for practical courses are tried and tested so well that compliance with the operating instructions guarantees safe and expedient work.

Most of these introductory texts also comprise fundamental treatises on safety issues in the chemical lab. However, many bibliographical references do not comprise specific and unambiguous safety advice. In case of doubt, address the instructor or assistant in charge.

However, one should also get accustomed to contemplating possible dangers and to consult further sources of information (hazardous substance databases on the internet such as GESTIS or GiSChem see Annex D) on one’s own initiative.

The labels of the original packaging of chemicals as provided by the supplier provide important information on volatility, flammability, acidity, capacity for autooxidation or spontaneous decomposition as well as other properties. Annex C will inform you about hazard symbols and warnings used as well as about alerts to particular dangers and special safety advice.

Due to amended regulations relating to classification and labelling, containers may be labelled in accordance with either the previous substance or preparation guideline or with the new CLP (Classification, Labelling and Packaging) regulation. For examples, please see pictures 1 and 2.

Such properties may also be inferred from analogy based on the chemical similarity to known substances.

Even though with regard to toxicological properties analogies may be misleading (benzene may cause leukaemia, toluene may not), but for some groups of substances they do provide a first hint even where toxicology is concerned.

For example, when working with alkylating reagents, the danger of potentially cancerogenic effects must be kept in mind. Read more about this in Chapter 9 Health Hazards and the compilation Frequently occurring hazardous substances, health hazards arising from them and suitable First Aid measures in section 11.3.

The literature annex lists a number of important books and data sheet collections providing important safety-related information. Find out about the availability of the referred literature in the library, and learn how to use it. Catalogues of chemicals also inform about many important substance properties. Hazardous material databases are available on the internet.

If it should be necessary to work with substances for which there is no information

Cat.:27,100-4 Lot.:GUVV-2005 Cont.:200 L

ALDRICH

Acetonitril, wasserfrei, 99,8%
Acetonitrile, anhydrous, 99,8%

CH_3CN

FG 41.05

CAS 75-05-8 EC200-835-2 Flap5 WGK 2 CH-Gift2 d0.786 Store at RT

EC-Label

For R&D use only. Not for drug, household or other use.

Sigma-Aldrich Chemie GmbH, Riedstr. 2, D-89555 Steinheim, Germany, Tel.: ++49 / (0)7329 / 97-0

SI07789037

1.00030.2500 29.02.12 2.5 l

LiChrosolv®
Reag. Ph Eur
Acetonitrile
gradient grade for liquid chromatography
Acetonitril
Acétonitrile
Acetonitrilo

Pictures 1 and 2: Manufacturer's labels on original packages available, they must be considered as dangerous. Inhalation and skin contact are to be avoided, and provisions for the case of decomposition must be made as required.

2.3 Essentials to be known and observed

While in a chemical lab, permanently wear protective goggles with side protection.

When performing work posing an increased hazard to the eyes, they must be replaced with fully closed and tight-fitting goggles (also known as basket goggles) or supplemented with a face shield.

For work putting the hands at risk, chemically resistant and mechanically robust protective gloves must be worn. Many hazardous substances are capable of diffusing into the material of the gloves, sometimes with amazing rapidity. Thus, substances such as acetone or xylene permeate various glove materials very quickly. Therefore the protective gloves must be selected according to the resistance data furnished by the manufacturer. In order to avoid contamination, do not touch light switches, door handles, taps at the washing basin, telephones, keyboards, writing utensils or the like.

2.3.1 Body protection and working clothes

In laboratories, appropriate **working clothes** must be worn any time. For normal laboratory work, this is a sufficiently long lab coat with long tight-fitting with a tissue cotton content of at least 35% (see picture 3). The lab coat must not be worn in lecture rooms, libraries, cafeterias etc.

The footwear must be robust and closed.

In situations of increased danger of fire, e. g. when decanting larger amounts of

Picture 3

flammable liquids, **protective clothing** of cotton with flame-retardant impregnation or flame-resistant special tissues must be worn. When handling larger amounts of corrosive liquids, liquid-tight protective clothing, e. g. a PVC apron, is to be worn.

Change from normal lab clothing to streetwear and back must be performed outside the lab (see picture 4). Any clothing contaminated with chemicals must be changed immediately.

Picture 4

2.3.2 Presence at the workplace

Anybody performing an experiment must not leave the station unless permanent supervision is unnecessary, or unless a colleague informed about the experimental procedures shall continue supervision.
For dangerous work, at least two persons must be present.

2.3.3 Food, drink and smoking

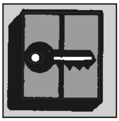
Because of the danger of contamination, food and drink may be neither stored nor consumed at the workplace. Even outside the lab, food and drink must not be stored in lab vessels or chemicals containers. Neither may chemicals be stored in vessels usually used for holding food and drink.
Smoking is not permissible in a chemical laboratory.

2.3.4 Cleaning and prophylactic skin care

After completion of the lab work, the hands are to be washed thoroughly each time with water and detergents gentle on the skin. For hands burdened with contact with chemicals or frequent washing, regeneration-promoting skin care with a rich cream is recommended.

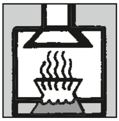
3 Handling chemicals

This chapter shows how to avoid contamination with chemical substances, danger to persons and, generally, the arising of dangerous situations when handling chemicals.
It describes the legal basis for handling chemicals and answers the following questions:



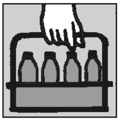
How to handle chemicals?

Which vessels and containers are appropriate to that purpose?



When must chemicals be stored in a fume hood or treated specially?

How to avoid mix-ups?



How are vessels or containers for chemicals transported safely?

How to avoid spilling or skin contact when decanting or metering chemicals?

How to deal with spilled chemicals?

3.1 Legal basis: Chemicals Act and Ordinance on Hazardous Substances

§ The Act on Protection from Hazardous Substances (Chemicals Act, Gesetz zum Schutz vor gefährlichen Stoffen or Chemikaliengesetz) is intended to protect persons and environment from noxious effects of hazardous substances and compositions, in particular, to make such substances detectable, to avert them and to prevent their formation. The Chemicals Act is also intended to ensure that novel chemicals are sufficiently examined for dangerous properties prior to marketing, and that in handling these substances the safety measures necessitated by the results of these examinations will be complied with.

The scope of the prescribed safety-related and toxicological examinations depends on the amount of the substance to be marketed. The labelling of the substances, i. e. the type of symbols, hazard warnings and safety advice on the labels (cf. pictures 1 and 2 and Annex C) depend on the results of the examinations. Usage limitations and other restrictions may also be imposed by the authorities.

The Ordinance on Hazardous Substances (Gefahrstoffverordnung), essentially based on the Workplace Safety Act (Arbeitsschutzgesetz) and the Chemicals Act, regulates all activities pertaining to hazardous substances, i. e. their production, storage and use. This ordinance further regulates classification and labelling of hazardous substances.

The purpose of the Ordinance on Hazardous Substances is to protect both persons and environment from damage caused by chemicals. The Ordinance on Hazardous Substances applies both to commercial industry and to offices, schools and universities and addresses the employer and all employees in the business. Officials, pupils, students and all other persons working at universities (e. g. scholarship holders) are considered as employees by the Ordinance on Hazardous Substances.

Assessment of danger

According to § 7 of the Ordinance on Hazardous Substances, the laboratory manager or course supervisor must first ascertain whether the employees and students are going to work with hazardous substances, or whether hazardous substances may be produced or released in the course of their work. In this case, as it is in the chemical laboratory, the dangers for the health and safety of the employees must be considered from the following perspectives:

1. dangerous properties of substances and compositions;
2. manufacturer's or vendor's information relating to health protection and safety, in particular material safety data sheets (MSDS) in accordance with § 6 of the Ordinance on Hazardous Substances;
3. degree, type and duration of exposition, taking into account all ways of exposition;
4. physical-chemical effects;
5. possibilities of substitution;
6. working conditions and procedures including instruments and amount of the hazardous substance;
7. workplace limit value and biological limit values;
8. efficacy of protective measures implemented or to be implemented;
9. conclusions from previously conducted occupational health examinations.

The laboratory manager or course supervisor may permit work with hazardous substances only after performing this assessment of danger and implementing appropriate protective measures. It must be the goal of these measures to comply with workplace limit values and to minimize exposition of employees to hazardous substances. In chemical laboratories these goals can be considered as met if

- work is performed using the small amounts of substances which are regularly used in the lab;
- all work with toxic, very toxic, cancerogenic, mutagenic and reproduction-toxic substances is performed in a fume hood and the fume hood is kept closed unless the equipment therein is being manipulated;
- the laboratories and course rooms are not overcrowded;
- dispensers and compressed gas cylinders for toxic and very toxic substances are placed within the hood;
- toxic, very toxic or corrosive gases and vapours released during reactions are removed by cryotraps or absorption solutions;

- contact with substances which may be absorbed through or are harmful to the skin is avoided by the procedure (e. g. use of closed apparatus) or appropriate personal protective equipment (protective gloves, goggles and face protection as required);
- personal work hygiene is paid attention to.

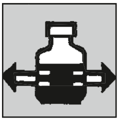
The Ordinance on Hazardous Substances is substantiated by a number of Technical Regulations for Hazardous Substances (Technische Regeln für Gefahrstoffe, TRGS). In particular, the TRGS 526 «Laboratorien» is to be named here. Further information relating to laboratories is to be found in «Sicheres Arbeiten in Laboratorien» (BGI/GUV-I 850-0).

For universities in particular, the «Umgang mit Gefahrstoffen im Hochschulbereich» (GUV-SR 2005), is relevant.

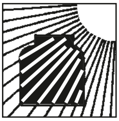
The information below takes into account the rules, regulations and explanations given above.

3.2 Storage and transport

Chemicals should remain in the original containers if possible since their legally required labels contain important information on safe handling, see section 2.2. Other containers must be labelled carefully and unambiguously after removal of any obsolete labels; labels must be covered with transparent film. Quick-and-dirty labelling with fibre pens is not permissible for storage containers because they are not durable enough.



All containers holding chemicals must be made of suitable materials. When storing organic solvents in plastic containers, the possibility of diffusion or embrittlement must be considered.



Some substances may change under the influence of light. They must be stored in opaque containers.

Avoid unnecessary storage of materials exceeding the amounts constantly required and provided for scheduled experiments.

All chemicals and preparations provided in the laboratory, as well as their containers, are to be checked for proper condition at least once a year. Chemicals and preparations in containers which do no longer conform to the regulations must be decanted into other containers or discarded, respectively, if no longer needed or unusable.

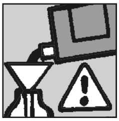
Chemicals which may release toxic, corrosive or flammable vapours or dusts may be handled only in a fume hood and may be provided only in small quantities. They must not be transported in an elevator together with persons.

When transporting glass containers, there is always danger of breakage. Bottles must never be carried by gripping their neck. Glass containers must always be transported in buckets, racks or, preferably, baskets or trays on wheels, see picture 5.

The dangers of fire and explosions in the storage of chemicals is discussed in section 6.1 – Flammable liquids.

Picture 5

3.3 Dispensing and decanting



Any decanting of chemicals presents danger of spilling, also upon skin and clothing, of inhalation of vapours or dusts and of formation of ignitable mixtures.

There are some rules which apply to decanting of smaller amounts in the lab, observance whereof essentially excludes dangers:

- When directly decanting, always use funnels for liquids or powders, respectively, even if personal dexterity would allow subjectively safe decanting without these implements.
- For decanting of liquids, in particular with toxic or corrosive properties (use a fume hood!), it is useful to place beneath a trough; for solids, a paper mat.
- The sizes of storage container, funnel and receptacle must match. For taking small amounts of liquids, a sufficient number of Mohr pipettes should always be available at the station.

- It is strictly prohibited to pipette liquids by oral suction. A variety of pipetting aids are available to that purpose, see picture 6.

- 

  When decanting liquids from a bottle, hold the bottle so that the label is upside when the bottle is in horizontal position so

Picture 6

that adhering drops cannot damage the label when running down the outside of the bottle. It is expedient to remove the adherent drop with the stopper of the bottle after decanting.

- Never place the stopper of the bottle with its lower section upon a table.

- Solids may be taken from the powder containers only using a clean spatula or spoon.

- Chemicals once taken from a storage container must never be returned to this container since otherwise the entire supply may be contaminated.

3.4 General safety precautions in experimenting

All experiments must be planned and prepared carefully. Appropriate preparation can be based on an Operating Procedure (see example on pages 19/20) which not only outlines the reaction equation and the description of the experiment but also comprises the characterization of the substances used and produced, hazards for persons and environment, protective measures and directives, actions to be taken in case of danger, First Aid measures and data relating to disposal.

Furthermore, prior to starting the experiment it must be made sure that the available time is sufficient for the entire work flow, otherwise breakpoints must be established in advance where the experiment can be interrupted without danger.

If it is necessary to have an experiment running for a longer time or overnight without supervision, appropriate safety measures must be taken in cooperation with the instructor or assistant in charge (e. g. increased fire protection, proper set-

OPERATING PROCEDURE

in accordance with § 14 of the Ordinance on Hazardous Substances
for chemical and related laboratories of the University of Bonn

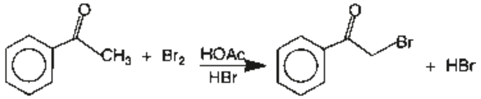
EXPERIMENTAL PROTOCOL

Name		First Name	Station	Course	Assistant
Doe		John	202	OC-1	A. Nonymus

To be produced: phenacyl bromide, 2-bromoacetophenone   Scale: 0.1 Mol

Literature: Reaktionen und Synthesen, Tietze, Eicher – Thieme 1981 – page 44

Reaction equation



Substances used, products	CAS #	MW	melting P boiling P °C	Hazard symbol and designation	R and S phrase #	Amount required for experiment
Acetophenone	98-86-2	120.2	BP 202	Xn, harmful	R22, R36, S26	12.0 g
Bromine	7726-95-6	159.8	BP 58.8	T+,C,N highly toxic, toxic, corrosive harmful to the environment	R26, R35, R50 S7/9, S26, S45, S61	16.0 g
Glacial acetic acid	64-19-7	60.1	BP 118.1	C, corrosive S26, S45	R10, R35, S23.2	10.0 ml
HBr solution, 48 %	10035-10-6	80.9		C, corrosive	R34, R37, S7/9, S26, S45 S36/37/38	1 drop
Phenacyl bromide	70-11-1	199.1	MP 47–48	Xi, irritant	R36/37/38, S24/25	

R and S phrases referred to above:

R10	Flammable	R50	Very toxic to aquatic organisms
R22	Harmful if swallowed	S7/9	Keep container tightly closed in a well-ventilated place
R26	Very toxic by inhalation	S23.2	Do not breathe fumes
R34	Causes burns	S24/25	Avoid contact with skin and eyes
R35	Causes severe burns	S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
R36	Irritating to eyes	S36/37/39	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
R37	Irritating to respiratory system	S45	In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
R36/37/38	Irritating to eyes, respiratory system and skin	S61	Avoid release to the environment. Refer to special instructions/safety data sheet

Description of the experiment (with equipment et up as sketched)
Equipment: 100 ml two-necked flask, dropping funnel with pressure compensator, internal thermometer, magnetic stirrer, ice bath.
To dissolve 12 g of acetophenone in 10 ml of glacial acetic acid containing one drop of 48 % hydrobromic acid, add 16 g of bromine under stirring and cooling with ice so that the temperature of the reaction mixture does not exceed 20 °C. Then stir for 20 minutes at room temperature. Then draw a sample of approx. 1 ml of the solution, rub it with glass rod to induce crystallization and add the seed crystals to the reaction mixture cooled to 3–4 °C; phenacyl bromide will precipitate in crystalline form. Aspirate and wash several times with a total of 40 ml of EtOH/H2O 1 : 1.Theoretical yield after vacuum drying: 10 g (50 %), colourless crystals, melting point 47–48 °C.

OPERATING PROCEDURE

in accordance with § 14 of the Ordinance on Hazardous Substances
Substance data see experimental protocol

Dangers for persons and environment

Bromine – is very toxic upon inhalation, causes severe burns and irritates the eyes and airways; hazardous to water (water hazard class 2).
Glacial acetic acid – highly corrosive to eyes, skin and airways; flammable and slightly hazardous to water (water hazard class 1).
Acetophenone – irritates the eyes; slightly hazardous to water (water hazard class 1).
Phenacyl bromide – irritates skin, airways and in particular the eyes; strong lacrimant; severely hazardous to water (water hazard class 3).
48 % HBr solution – highly corrosive to eyes and eyes, irritates the airways; preparation slightly hazardous to water (water hazard class 1).

Protective measures and directives

Perform all work in the hood, keeping the sash closed whenever possible. Wear laboratory gloves of rubber or plastic. Keep glacial acetic acid away from ignition sources (flashpoint 40 °C). When working with bromine, keep 3 % aqueous sodium thiosulphate solution at hand close to the apparatus.

In case of danger (emergency call 112)

After spilling of chemicals, in case of fire and after contact of chemicals with eye/skin, immediately inform the assistant.

Bromine: Let splatters evaporate in the hood or react them with 3 % sodium thiosulphate solution. Absorb larger amounts with absorbent.

Glacial acetic acid/HBr solution: Remove splatters with water, absorb larger amounts with moisture-binding material and clean with water afterwards; extinguish acetic acid fires with carbon dioxide or powder.

First Aid (First Aiders: all assistants)

After contact with eyes: For all substances used and for phenacyl bromide, rinse eyes with plenty of water for at least 15 minutes; consult ophthalmologist if necessary.

After contact with skin: Wash skin wetted with bromine immediately with 3 % sodium thiosulphate solution and then with plenty of water; consult physician if required.

After inhalation: For all substances used: fresh air; consult physician if required.

After contact with clothing: Immediately take off wetted clothing.

Correct disposal

Rinse all equipment that has come into contact with bromine with sodium thiosulphate solution. The rinsing solution can be discarded as waste water. Neutralize all solutions comprising organic solvents and discard into the container for solvent wastes.

Preparation approved for synthesis with the amounts calculated on the recto side.

Signature of assistant

Chemicals handed out: signature chemical storage

Own observations during performance of the reaction, reaction mechanism and literature data and findings (such as yield, melting point, boiling point, refractory index) are to be recorded separately.
Use separate sheet; data in header as on first page.

ting of control and regulation devices, safe shut-down in case of electricity blackout).

Availability of all chemicals and devices required must be made sure prior to beginning the experiment. A search for missing materials will inevitable lead to hurry and thus to an increased safety risk, particularly during difficult phases of an experiment.

By preparing an experiment on the day before, time and flexibility are gained.

The following safety precautions must always be observed:

- Chemicals must not be brought into contact with the skin and therefore must not be touched either.

- Use hazardous substances in small amounts only. The more dangerous a substance used or produced, the smaller the scale should be.

- When heating liquids, superheating (bumping) must be avoided by stirring, use of boiling chips or granules, boiling capillaries, etc. Test tubes must be shaken permanently, since otherwise the entire liquid may squirt out as a result of sudden boiling. Never point the opening of a test tube towards you or any other person!

- Work which may produce dangerous amounts or concentrations of gases, vapours or aerosols must always be performed in a fume hood. Such activities comprise evaporation or fuming off as well as heating of oil baths in distillation processes.

- During such work, the front sliders (sashes) and movable panes are to be kept closed if possible (see pictures 7 and 8). Work with the front slider opened is permissible only exceptionally and for cause, since in this case release of noxious matter will be higher, and the user will not be protected from squirting of hazardous substances or from shattered glass fragments. However, in any case the head should be kept in the area protected by the pane.

- Operating Bunsen burners in the hood can significantly disturb the air flow, and they should therefor be used only to the degree they are absolutely required.

- Likewise, the efficacy of the hood is strongly affected by obstructions of the air flow, e. g. standing bottles or devices. Therefore, hoods should be kept as free as possible. Do not abuse hoods for the storage of chemicals or for installation of large equipment requiring ventilation (muffle kilns, drying cabinets etc.)!

- For workplace safety and environment protection, hazardous substances released in the hood are to be collected at their site of release or formation if possible and removed e.g. by absorption (see residual gas scrubbing, picture 7).

- When using a rotary evaporator (also known as Rotavap or Büchi), appropriate setting of the temperature of the water bath and of the vacuum will result in good condensation. Regulated rotation pumps or membrane pumps are tried and tested, and in comparison to water aspirators they have the advantage of reducing waste water production and preventing water pollution. The solvents trapped in the condensate collector can be partly re-utilized by distillation or collected for disposal.

- Squirted or spilled chemicals must be appropriately disposed of at once. Concentrated acids or bases are neutralized, then the liquid is wiped off. In doing so, protective gloves must be worn. Hazardous liquids are ideally absorbed with suitable absorption granulates (for strong oxidants such as concentrated HNO_3 or $HClO_4$ use mineral absorbents only; do not use synthetic resin absorbers!). The used granulate is collected into plastic bags and disposed of as toxic waste.

Picture 7

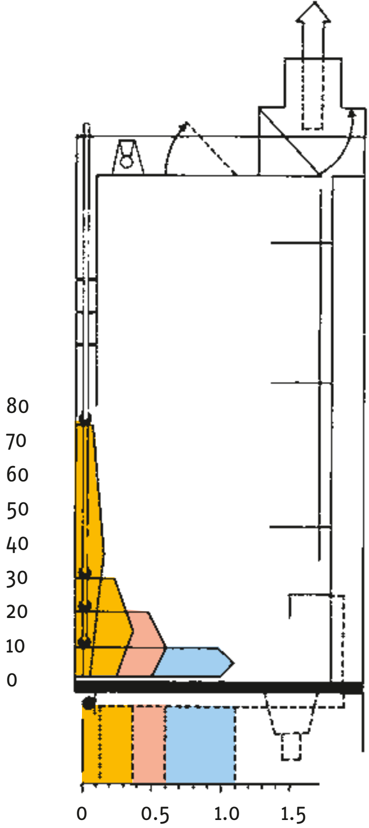
Conventional fume hood with vertical sash and external air supply.

- Always keep the sash closed when the hood is not in use or the installed equipment presently does not require hands-on work.
- When working with any equipment, do not open the sash any further than absolutely required; the head should always be in the area protected by the pane.
- The ventilation effect is highest when the sash is lowered, since then the speed of the air flow in the aperture is highest!

Efficacy of a fume hood in relation to the aperture of the sash:

If the speed of the air flow is below 0.5 m/s, there is the inevitable danger that persons passing by will extract noxious matter from below the hood by the air turbulence they cause.

In modern hoods with electronic regulation there are many different embodiments. Here instruction by the technical service or an appropriately trained person (e. g. course assistant) is required. Control circuits which the user perceives as distracting must not be unplugged or reset at any rate! The basic rules for fume hoods as described above apply here as well.



Picture 8

3.5 Safety measures for experimenting with special chemicals

Acids and bases

Because of the heat released in the process, caution is advised when diluting concentrated acids with water and when dissolving solid alkali hydroxides. Concentrated acids (sulphuric acid in particular) are to be added slowly to water, not contrariwise, under stirring. Lyes and highly basic amines, in particular higher alkylamines, have an even stronger corrosive effect on eyes and skin than acids.

Hydrogen fluoride

Work with anhydrous hydrogen fluoride and/or hydrofluoric acid may be performed only in a fume hood. In addition to protective goggles, a protective shield, long protective gloves or, if required, a full mask must be worn. Because of the highly corrosive and toxic effects, inhalation and skin contact with this substance must be avoided at any cost. If inhalation or skin contact occurs nevertheless, swift First Aid is of paramount importance, see section 11.3!

Perchloric acid, azides, permanganates

In the presence of oxidizable substances, anhydrous perchloric acid, perchlorates and chlorates tend to explode, and azides are prone to spontaneous decomposition. Chlorates and permanganates may also cause explosions when concentrated sulphuric acid is added.

Alkali cyanides

Alkali cyanides react with acids to form hydrogen cyanide (prussic acid). Therefore these materials must not be discarded into the sink (see also section 5.2, Disposal of laboratory wastes).

Mercury

When handling mercury, it must be made sure that nobody will be exposed to mercury vapours. Spilled mercury is to be rendered harmless immediately, either by collecting with a mercury pincer or by aspiration into a mercury pipette or by chemical reaction with iodated coal or Mercurisorb® (see also section 5.2).

Ether

For the avoidance of explosions when distilling ether-containing solutions, caused by peroxides contained therein, it is required to store ether always in brown bottles over KOH pellets. The residues must never be distilled off!

A test for peroxide contents may be performed using special test sticks or reagents (e. g. titanium(IV) sulphate or potassium iodide). Peroxides can be removed using iron(II) sulphate.

Sodium

Sodium residues are removed as described in section 5.2. Because of the release of hydrogen resulting in danger of explosions, sodium must not be thrown into water!

Explosive silver compounds
When working with solutions containing ammonia and silver salts, it is to be kept in mind that after a while a black precipitate will be formed which partly consists of explosive silver compounds and may detonate violently upon touching, stirring or shaking.

Caution:
This list is not complete!

4 Chemical equipment

This chapters shows how to set up equipment expediently for safe and reliable operations.

It answers the following questions:

1. **How to handle glassware without danger of injury**
2. **How to separate stuck glass connectors**
3. **Which tools to use for circumvention of dangerous manipulations on glassware**
4. **How to set up equipment expediently, stably and shatter-proof**
5. **How to make possible flexible handling of equipment during operations**
6. **Dangers from electromechanical tools**
7. **Risks in heating and cooling of equipment**
8. **The most appropriate heating and cooling instruments**
9. **Special safety measures for work under reduced pressure**
10. **How to handle pressurized gas cylinders**
11. **How to secure equipment which gases are to be fed into**
12. **How to avoid leakage of toxic or corrosive gases**

4.1 Handling laboratory glassware

Equipment in chemical laboratories consists mostly of glass. In spite of all the advantages which this material has for chemical work, its fragility poses a danger. Injury from broken glassware with sometimes severe lacerations is among the most frequent laboratory accidents. Therefore in handling glassware it is of paramount importance to check all glassware for integrity prior to use and to avoid any violent handling. Basic training in the techniques of glass-blowing provides the chemist with the required skills in handling glassware.

The following information is intended to show how to avoid situations leading to breakage and injury.

Breakage in placing and jolting
Position the glassware carefully, do not bang it against the laboratory table, do not place it upon uneven locations. Punctual forces, such as grains of sand on tables, are dangerous for glassware.

Breakage by twisting or bending
Glass is broken easily, therefore always grip closely to the centre of gravity (short lever). Do not use protruding ends (T pieces, bends of cooling devices etc.) as levers when handling.

Cutting at sharp edges
Partially fractured edges of glassware result in injury from sharp borders. Such glassware must not be used any longer.

Breakage when introducing glass tubes, glass rods or thermometers into the bore of a stopper or when mounting hoses on the glass adaptors of cooling devices or vacuum flasks
Try to avoid breakage by greasing the glass surface with glycerine, followed by introduction of the glass object with slightly twisting movements with as short a lever as possible. In addition, protect the hands by wrapping a towel around them (see picture 9). Screw closure bores offer more safety.

Picture 9

Removal of stuck hoses
Cut off such hoses and carefully remove the residues from the glass using a sharp knife.

Detachment of stuck ground glass connectors
Warm the ground glass connector using a hair dryer (causing the bushing to expand more quickly than the core), until the connector can be detached easily using twisting movements (with your hands protected!). As a remedy, use e. g. teflon bushings or highly fluorinated fats in lieu of vacuum grease.

4.2 Setting up chemical equipment

Breakage of equipment is among the greatest risks of chemical laboratory practice, in particular because this may lead to fire or to release of hazardous substances. Therefore, several important safety principles must be observed as early as during the set-up of an apparatus.

Avoid any improvisation resulting from usage of inappropriate parts.

Equipment must be installed stably, free from tensions and at safe locations. Ideally, they are fixed using clamps and sockets on stationary struts. If individual (movable) struts must be used, the apparatus is to be centred above the centre of gravity, i. e. above the base plate of the strut. Wobbly struts must not be used.

No excess pressure must be able to build up in the equipment (with the exception of pressurized reactors); therefore the equipment must comprise an expansion valve for equalizing pressure with the external atmosphere.

The contents of the apparatus may be protected from atmospheric moisture by using drying tubes, necessitating the use of drying materials which cannot cake and clog the tube (e. g. drying materials on carriers) nor react with chemicals of the reaction (e. g. no $CaCl_2$ when working with amines).

Equipment is essentially set up vertically. First fix the reaction vessel (or the distillation flask etc.) safely. Position it considering that heating and cooling baths must be removable without modifications to the apparatus. Add further components of the apparatus by attaching them to the adaptors of the flask and securing them with clamps. In clamping, neither loosen ground glass connectors nor cause tensions by tilting. Agitator shafts in particular must be connected tightly and safely to the reaction vessel.

Electrical equipment must be in impeccable technical condition. Devices with damaged cables, plugs or contacts must be removed and repaired by a specialist. Home-made devices in particular must be controlled for operating safety by a specialist in accordance with the relevant regulations.

The functioning of equipment, e. g. of the cooling water system, agitators, electrical motors, vacuum tightness, must be verified before loading any apparatus with chemicals. Hoses must be attached safely (e. g. using clamps).

4.3 Heating of equipment

Chemical reactions pose a particular hazard when working at elevated temperature, especially when heating flammable solvents. The following information is intended to avoid the resulting risks.

All heated apparatuses with flammable contents must be equipped with condensers for the retention of volatile, flammable substances.

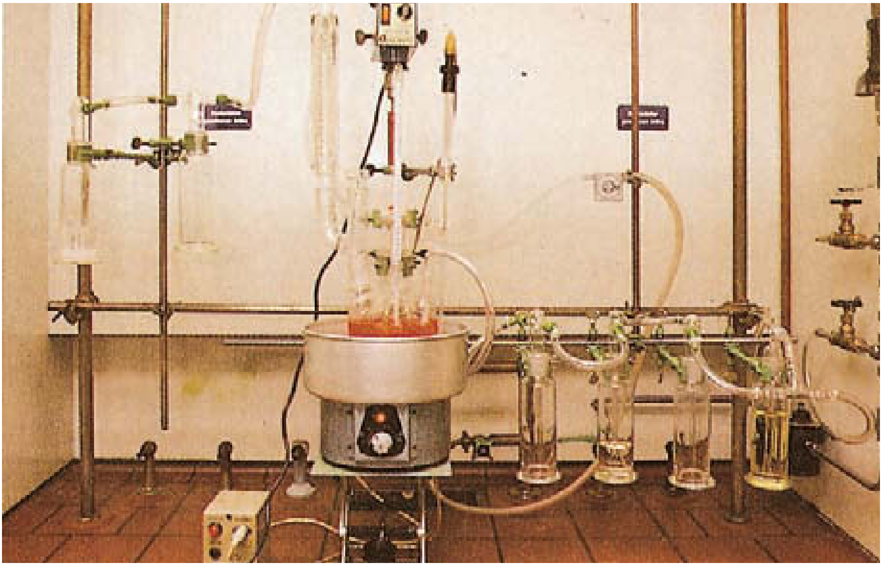
Heat sources must always be attached in such a way that they can be removed without modification of the apparatus. Laboratory hoisting platforms are best-suited to this purpose (see pictures 10 and 11).

Equipment containing flammable or thermally labile substances must never be heated directly with an open flame, not even above a wire net or sand-bath. Direct heating in the air bath with an electric heating mantle is possible but recommended only when uniform distribution of the heat is guaranteed, e. g. by stirring.

Uniform boiling of liquids must be guaranteed by adding boiling chips or permanently stirring since otherwise superheating and violent bumping must be expected.

The safest heating method is to use liquid heating baths, rendering possible heat transfer at low temperature differences.

Heating baths with gas burners may be used only in combination with non-flam-



Picture 10

Picture 11

mable liquids and under constant supervision. Continuously variable electric heating plates are preferred and generally applicable. For equipment intended to run without supervision, self-regulating systems with thermostatic control of the heating bath are indispensable. Protection from superheating is required to guard against the consequences of a failure of the regulatory unit.

Water baths can be overlaid with a thin paraffin film to protect them from drying up. They must not be used if the apparatus contains alkali metals, their hydrides or other substances which may react violently with water.

Heating bath liquids have a maximum operating temperature, above which they may decompose and form noxious vapours or even inflame.

Hot heating baths are dangerous. They must be set up to be safe from tilting. Significant volume expansion of the liquid during heating must be anticipated.

Infiltration of water can lead to violent squirting of the hot bath liquid. Therefore cooling water adaptors above oil baths must be checked for tightness. Dripping down of condensed water must be prevented by attaching a paper collar.

Heating using a hot-air blower
When baking out equipment, make sure there are no flammable liquids in the danger zone. The hot-air blower may be set down only at a safe location outside the hood.

4.4 Cooling

For cooling, ice, ice/salt mixtures (sodium chloride down to approx. −21 °C, calcium chloride down to approx. −55 °C), solvent/dry ice mixtures (down to −78 °C) or liquid nitrogen (−196 °C) are used. Dewar vessels, frequently used for isolation, are inwardly reflective hollow glass structures and thus in danger of implosion. Only vessels equipped with protective cleading may be used; avoid mechanical stress (mind the immersion depth!). Today, highly isolated metal Dewar vessels are commercially available which do not pose a danger of implosion. In many cases, Dewars may be replaced with breakage-proof vessels of foam plastic.

For dry ice cooling, flammable organic solvents are frequently used as transfer media. The resulting fire hazard is to be kept in mind; open fire must be kept off. Frequently used media are acetone or methanol. Isopropanol, however, is recommended; its advantages are its low toxicity and its high viscosity which prevents squirting when dry ice is added.

For deep cooling, liquid nitrogen (boiling point −196 °C) is used. After prolonged periods of time, atmospheric oxygen may be absorbed, which becomes visible by the blue colour. Because of the high oxidative potential of liquid oxygen, such mixtures may no longer be used. They should be destroyed by evaporation, e. g. by pouring out outdoors.

4.5 Special information

Stirrers and centrifuges
Never reach into equipment in motion. Stirrers or centrifuges must be powered up or down slowly and gradually. In case of unusual noises, immediately turn off and inspect.

Sand baths
Calcined sea or river sand is suitable for filling. Replace contaminated sand at once. Sand baths may be used only if the non-uniform temperature distribution occurring therein, especially during continued heating, does not result in any hazard.

Devices for melting point determination
These devices must not be filled with concentrated sulphuric acid. Suitable bath liquids are, e. g., silicone oils. Metal block or electrically heated liquid melting point determination devices are recommended.

Drying cabinets
Products which upon drying may release flammable gases or vapours must not be dried in drying cabinets without explosion protection.

Refrigerators
Flammable liquids may be stored only in refrigerators whose inside is explosion-proof. Pay attention to storing the vessels in an upright position and secured against tilting; stoppers, plugs and the like are to be secured (see picture 12).

4.6. Special methods

4.6.1 Work under reduced pressure

In chemical laboratories work is frequently performed under reduced pressure.

Typical examples comprise distillation or sublimation in vacuum, aspiration of precipitates, drying. The equipment used to these ends must resist considerable strain by external pressure.

With the vacuum connected, the pressure load amounts to approximately 1000 hPa (= 100’000 pascals = 100’000 N/m^2 glass surface), almost independent of the pump used.

It is a popular fallacy that work under water aspiration vacuum is harmless in comparison to high vacuum. In fact, the pressure strains differ only by 10 – 20 hPa (1000 – 2000 pascals). Even during aspiration of precipitates, the Büchner flask reaches strains of 300 – 800 hPa (30’000 – 80’000 pascals). Breakage due to strain under reduced pressure leads to implosion, and flying fragments may cause severe injury. Therefore it goes without saying that vacuum work in glass apparatuses must be performed with special caution and compliance with the safety rules.

When working under reduced pressure, sufficient protection is mandatory. If possible, the vacuum is to be limited to the degree required for the experiment. Vacuum regulation is recommended.

Use only glass equipment with undamaged surface (visual inspection!). Make sure there is no additional strain due to tensions caused by twisted fixing of apparatuses. Evacuated components must not be heated on one side only.

For work under reduced pressure, use glassware with convex surface only (e. g. round-bottomed flasks). Never use Erlenmeyer flasks or other flat-bottomed vessels. In deviation from this, thick-walled vessels specifically designed for vacuum work may be used (Büchner flasks, exsiccators). They must not be heated on one side only!

When aspirating, pay attention to good fitting of the rubber collars between the suction filter and the Büchner flask; sudden slippage of the collar may cause breaking of the flask.

Operate and store evacuated equipment only in locations protected from inadvertent tilting or dropping of objects.

Use of protective shields or wire baskets, especially for large-volume vacuum apparatuses, is an effective splinter protection in case of implosions. Exsiccators and Dewar vessels can be secured by covering the surface with transparent film (see picture 13). Plastic-covered equipment is also commercially available.

Picture 12: Consequences of using a fridge that was **not** explosion-proof

Picture 13

4.6.2 Working with gases

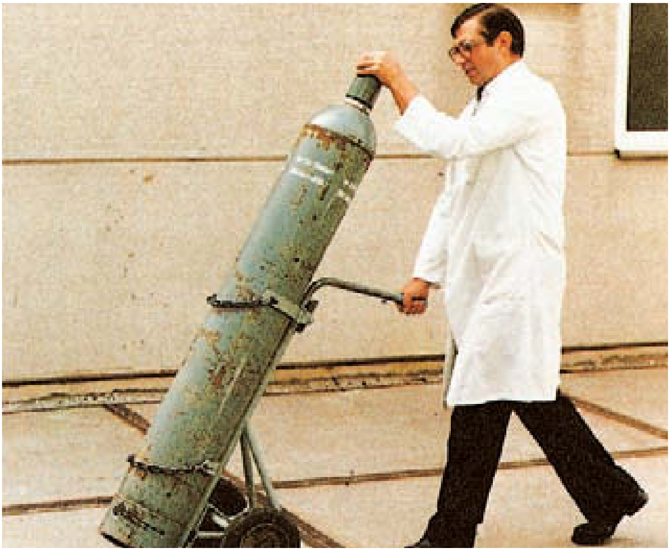
Gases are often used as starting materials or protective gases in chemical reactions or can be produced by chemical reactions. They are also used as auxiliary material in some analytic procedures. Handling of gases is always problematic: Gases will diffuse very quickly into the laboratory atmosphere, with flammable gases then easily forming ignitable mixtures, and toxic gases will endanger people already at very low concentrations. Special hazards result from work with gases under pressure.

4.6.3 Pressurized gas cylinders

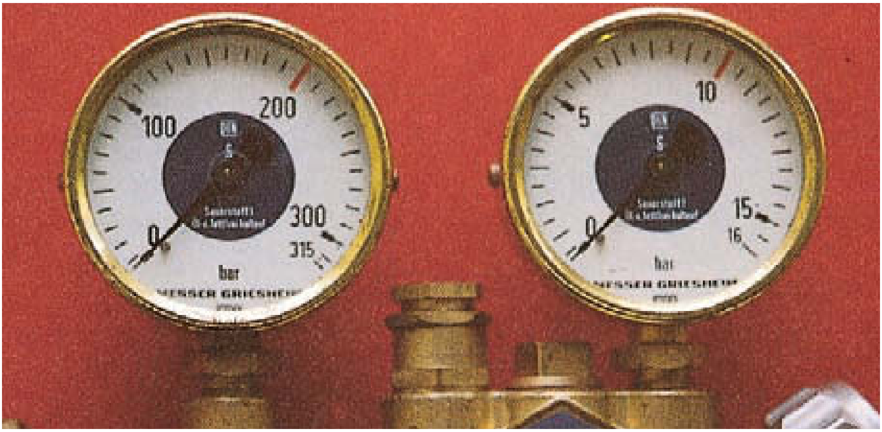
General issues

Most gases are marketed in compressed form (liquefied or under high pressure) in pressurized gas cylinders. Pressurized gas cylinders pose a hazard in their own right, since they may explode upon inappropriate handling (tilting, excessive heat). This leads to some mandatory safety rules.

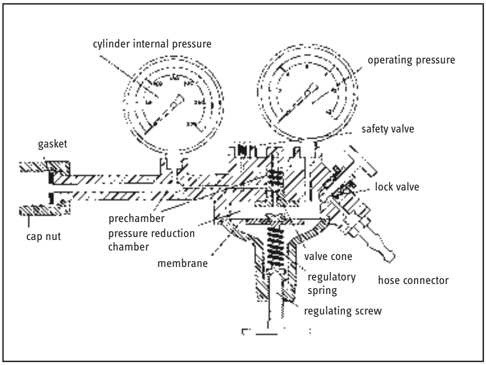
If possible, pressurized gas cylinders should not even be brought into the lab, since in case of fire they present an additional risk for fire-fighters. The safest possibility is to supply the laboratory from externally located cylinders via a pressurized pipeline. Storing the pressurized gas cylinders in lagged and ventilated lockers close to the station in the lab is likewise an effective measure. If none of these possibilities exist, pressurized gas cylinders may be brought to the station only for experiments and must be returned to the designated safe storage room immediately afterwards.



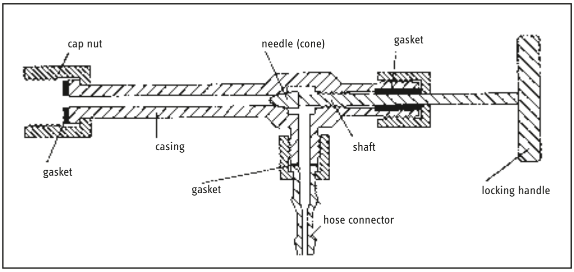
Picture 14:
Pressurized gas cylinders must be secured by chaining up against tilting both during transport on the carts designed for this purpose and on-site.



Picture 15



Picture 16: Design of a reducing regulator



Picture 17: Design of a needle valve

When the cylinder is not in use, its valve must be secured by screwing on the protective cup.

In the laboratory, toxic or corrosive gases should be used only in small cylinders which can be directly placed into a fume hood.

Operation and release

Behind the cylinder valve, pressurized gas cylinders feature a screw thread for mounting the release valve. If possible, reducing regulators must be used (see pictures 15 and 16). Needle valves are no reducing regulators, only flow restrictors (see picture 17). For this reason they should be used only in case no reducing regulators are available (e. g. for certain liquefied gases). Only release valves approved for the individual gas may be used. Valves may be installed by trained staff only. With strongly oxidizing gases, the valves must be kept free of oil, fat and glycerine.

For releasing gas, first open the main valve with the release valve still closed. If the main valve cannot be opened by hand, the cylinder must not be used and is to be returned to the specialists. Vice versa, the use of tools for closing the main valve is not permissible. (Stuck main valves are observed in particular with corrosive gases; just here inappropriate handling regularly results in dangerous situations.) Finally, for release the fine adjustment valve is opened carefully to adjust the gas flow desired.

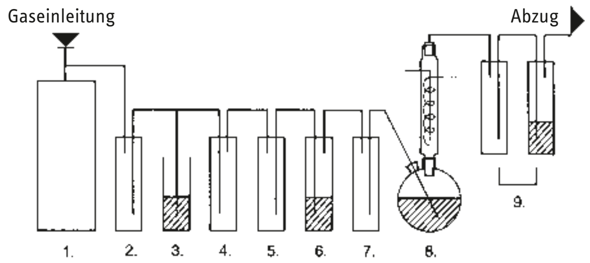
Needle valves for corrosive gases must be cleaned by flushing and blowing out immediately after completion of each individual experiment, since otherwise malfunction during the next operation may result.

Emptied cylinders should still have some residual pressure. They must be marked unambiguously as being emptied.

Feeding of gases

Gases are fed into reaction apparatuses via hoses secured with clamps, the hoses being resistant to the gas used (see picture 18). Silicone hoses are universally applicable. Gases may be fed into apparatuses only after it has been made sure that no excess pressure may be built up in the apparatus. A safety buckling is expedient, which offers the further advantage of preventing reflux of the reaction mixture to the gas cylinder and in particular mixing with drying liquids (e. g. concentrated sulphuric acid).

When feeding leads to solid reaction products, there is the danger of clogging of the feeding tube and uncontrolled build-up of pressure in the infeed system. Such reactions necessitate permanent observation. There are special feeding systems which allow mechanical removal of solids from the feeding tube without the need for opening the apparatus.



1. pressurized gas cylinder
2., 4., 5., 7. } empty vessels for buffering with feeding pipe (pay attention to proper fitting!)
3. dip leg (pressure relief trap)
6. washing liquid
8. reaction vessel with feeding pipe
9. residual gas scrubbing

Picture 18

All gas feeding systems must comprise a zero-pressure release aperture with a draining hose leading directly to the duct of the hood. A bubble counter inserted in between additionally allows to control gas absorption in the reaction.

The release of major amounts of unreacted toxic or corrosive gases into the hood system must be prevented. This is done by absorbing the gases into appropriate reaction media (e. g. diluted soda lye for phosgene). Such additional devices have the character of reaction apparatuses and must correspond to the same safety considerations as previously described. E. g., the amount of absorption solution must correspond to the gas volume expected; in exothermic reactions cooling must be provided, and care must be taken to ensure that the solubility of solids formed is not exceeded.

4.6.4 Working with autoclaves

Reactions under pressure may be performed only in suitable and approved pressure vessels (laboratory autoclaves, see picture 19a).

Picture 19a: Manual autoclave with hotplate stirrer

Pressure vessels must be designed, equipped, installed and operated in accordance with the regulations of the Ordinance on Industrial Safety and Health and the relevant technical rules.

Students may work with pressure vessels only after instruction and under supervision of the assistant in charge. In pressure vessels for experimental purposes, known reactions with pre-determined maximum degrees of filling may be performed, if the permitted maximum operating pressure and temperature are not exceeded. Expediently, prior to any operation of a pressure vessel the measurement devices for pressure and temperature and leak-tightness are checked. Both filling and emptying of the pressure vessels may be performed only in fume hoods or under local aspiration. Pressure vessels may not be opened before bleeding to atmosphere pressure levels.

For reactions under pressure where the pressures and temperatures to be expected are **not** reliably known, so called **experimental autoclaves** must be used. For the protection of persons, in particular in case of autoclave failure, the autoclaves must be installed in separate rooms (autoclave rooms). Observation of the measurement and safety devices must be performed from a safe place. During the operation of experimental autoclaves, pressure and temperature must be continuously monitored and recorded.

If there is any danger that the permissible operating temperatures or pressures are exceeded, the experiment must be stopped immediately (heating, off, emergency cooling if required).

After each use, or after completion of an experimental series if applicable, the autoclave must be examined by a competent person. If any damage should be found, or if permissible operating temperatures or pressures have been exceeded, the autoclave must be tested for further usability by an approved authority such as the Technical Supervisory Association (TÜV).

Glass autoclaves may be operated only in hoods complying with the norms or, preferably, in a separate autoclave room. The glass autoclave must be surrounded by a basket wire acting as splinter shield (see picture 19b).


Picture 19b: Glass autoclave with wire basket

Because of the high hazard potential of glass autoclaves, students should use metal autoclaves wherever possible!

4.6.5 Working with Carius tubes

Carius tubes (fused, thick-walled glass vessels) are a special form of pressure vessels. They can be used with reduced (vacuum) or increased internal pressure.

If the glass is damaged or of insufficient quality, reduced pressure may lead to implosions, and increased pressure to explosions. In both cases, destruction of the tube may result if reactions performed in the tube run away. When a reaction is performed in a Carius tube, only the external temperature can be determined directly, all other parameters may be calculated at best. Carius tubes are no approved pressure vessels (see item 4.6.4). Because of the inherent dangers they may be used only if they cannot be replaced with other, less dangerous equipment, e. g. for performing and observing chemical transport reactions.

Carius tubes of thick-walled (1 to 3 mm), chemically and thermally particularly resistant special glass can be used up to approximately 30 bar and 400 °C. However, above 300 °C water is strongly corrosive to glass. It is of particular importance that the tubes are fused without strain, and the portions of the tube which are exposed to the flame are not wetted with the chemicals filled in (use funnel for loading, pay attention to careful handling, freeze the contents prior to fusing if required).

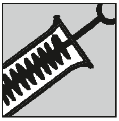
Loading and opening of the tubes must be performed in such a way that nobody's health can be affected by hazardous substances contained therein, i. e. in a fume hood! The most important protective measure is effective splinter protection (e. g. outer tubes of steel, wrapping into splinter-absorbing material, protective walls, separate room if applicable). Carius tubes may be opened only if it can be assumed that potential excess pressure has been reduced by cooling (do the calculation!). Even in this case use splinter protection, especially for the hands! The aperture thus formed must point away from the body.

Students may work with Carius tubes only after practical instruction and under permanent supervision by the assistant in charge. Fusing of the tubes should be done by a glass-blower.

5 Cleaning and disposal

5.1 Cleaning glassware

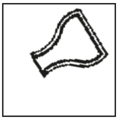
When cleaning glassware, there is danger of contamination with more or less unknown substances, e. g. by-products of a synthesis. Safe and expedient cleaning is done as follows:



Immediately clean contaminated vessels or other equipment. Do not allow residues to stand in vessels.

When cleaning, wear protective gloves and goggles. Beware of glass breakage and injury by cutting during mechanical cleaning. Remove grease using a paper towel and benzine if required.

Flush residual chemicals from the vessels using suitable, preferably non-toxic solvents (e. g. acetone, ethanol, benzine). Dispose of the rinsing fluid as special waste.
To avoid breakage, solvents should be stored close to the sink unit in plastic squirting bottles.



Do not place equipment rinsed with solvents into the drying cabinet for drying.

Aggressive cleaning agents (e. g. concentrated nitric acid, concentrated sulphuric acid) may be used only if other cleaning agents have been found useless.

Dichromate sulphuric acid may be used only exceptionally and for cause (for disposal, see section 5.2). Before usage, ascertain that the residual contents of the vessels cannot lead to hazardous reactions with the cleaning agent.

In many case, the aforesaid cleaning agents can be replaced with commercially available special detergents.

Only after pre-cleaning as described, cleaning with commercially available detergents is performed.

5.2 Disposal of laboratory wastes

All wastes must be disposed of. Disposal is regulated by the Act for Promoting Closed Substance Cycle Waste Management and Ensuring Environmentally Compatible Waste Disposal (Gesetz zur Förderung der Kreislaufwirtschaft und Sicherung der umweltverträglichen Beseitigung von Abfällen), a.k.a. Recycling and Disposal Act.

All wastes exempt from disposal by the municipalities must be properly disposed of by the owner; in accordance with the Ordinance on Documentation of Re-utilization and Disposal (Verordnung über Verwertungs- und Beseitigungsnachweise), proof must be furnished, e. g. for chemical special wastes.

The obligation to dispose of wastes should be self-evident to everybody handling chemicals even without legal regulations, since wrong handling may result in damage to persons, property and environment.

Disposal does not only mean to collect laboratory wastes and to dispose them jointly in accordance with internal guidelines, but also to avoid emissions and to convert various small amounts of wastes to harmless compounds by suitable chemical reactions. This chapter can only present a few hints in short form relating to the praxis of disposal in the laboratory and suggest to get familiar in any individual case, prior to beginning any work, with corresponding ways of disposal as well.

Organic solvent wastes are to be disposed generally. When collecting them, it must be kept in mind that in glass vessels only up to 5 l, in fracture-proof vessels only up to 10 l may be collected. Vessels with a nominal capacity of more than 5 l must be electrostatically conductive and grounded during decanting. Before pouring wastes into the collection container, a mixing experiment should be performed in the test tube.

Heavy metal salts and their solutions must be collected in separate containers.

Mercury wastes should be collected separately and recycled.

Filter and aspiration masses form a separate group, also comprising chromatographic plates and the contents of chromatographic columns. They are to be collected and disposed of separately.

Fine chemicals are sent to disposal in the original bottles.

In accordance with the Recycling and Disposal Act, waste oil from vacuum pumps and heating baths which is contaminated by laboratory work must be disposed of as strongly contaminated waste oil.

If in spite of the good detergents available today dichromate sulphuric acid must still be used, it is to be collected in separate containers and disposed of.

Disposal measures which may release noxious gases must be performed in a fume hood.

5.3 Disposal of minimal amounts

For minimal amounts of wastes, detoxification by the laboratory staff is often advisable or necessary.

Disposal of minimal amounts necessitates properly functioning hoods; it may be performed only by persons with appropriate know-how and in compliance with the protective measures required in the individual case.

The Operating Procedures are to be written carefully, and the executing persons (also and in particular including students!) are to be instructed in detail.

The Operating Procedures listed are carefully researched; however, the practitioner is under obligation to check and, if necessary in the individual case, modify the possibilities with regard to his product.

Alkali metals

Alkali metals are fed, under stirring, into a suitable alcohol (ethanol for sodium, isopropanol for potassium) which is provided in an inert solvent (e. g. petrol ether 40/60).

The apparatus used to this end consists of a multi-necked flask, a Dimroth condenser with metal cooling coil and a magnetic or sealed precision glass (KPG) stirrer. The hydrogen released is directly fed into the hood duct via a hose connected to the exit of the cooler. The alcoholate solution is hydrolysed, neutralized and finally disposed of as a solvent.

If there is sodium in wire form in the flask after drying a halogen-free solvent such as diethyl ether, cyclohexane or toluene, slowly and dropwise add the alcohol to the residue of the solvent remaining in the flask.

Prior to hydrolysis of the alcoholate, add several millilitres of a mixture of 1 part water and 4 parts alcohol to increase proton activity and remove residual traces of the alkali metal.

Bromine

Elementary bromine should primarily be recycled. Smaller amounts may be reduced with an aqueous solution of sodium thiosulphate to form bromide.

Hydrides

In a three-necked flask with stirrer and Dimroth condenser with metal cooling coil and dropping funnel, react alkali boron hydrides with ethanol, alkali hydrides and alkali amides with isopropanol from a dropping funnel. The hydrogen released is directly fed into the hood duct via a hose connected to the exit of the cooler.

Handling of lithium aluminium hydrides has resulted in a number of of accidents and fires. The following method of disposal is tried and tested and offers a high degree of safety.

In a three-necked flask with stirrer and Dimroth condenser with metal cooling coil and dropping funnel with pressure compensator, react the lithium aluminium hydride under inert atmosphere (argon or nitrogen) with ethyl acetate or acetone. The two reagents, which are converted to ethanol or isopropanol, respectively, during the reaction, prevent formation of hydrogen. The reagent solution should consist of 1 part of the reagent and 4 parts of ether; during adding, it should not come into contact with the wall of the flask to avoid formation of inclusion nests of unconverted lithium aluminium hydride.

Iodine

In analogy to bromine, elementary iodine is disposed of by reducing it with an aqueous solution of sodium thiosulphate.

Phosphorus, white
White phosphorous is pre-loaded into a multi-necked flask under inert gas. In the air stream subsequently conducted over the phosphorus, the latter burns. The oxides are neutralized in a collector containing an aqueous, alkaline solution.

Sulphuric acid, fuming (oleum)
Under cooling, the fuming sulphuric acid is slowly and dropwise added to 50 % sulphuric acid. This is then disposed of as a waste of the class Inorganic acids, acid mixtures, acidic etchants.

Acid chlorides, acid anhydrides
The compounds (e. g. thionyl chloride – $SOCl_2$, phosphorous pentachloride – PCl_5, chlorosulphonic acid – $ClSO_3H$, acetate anhydride) are added to 10 % sodium lye under good cooling. Disposal is then performed according to the resulting products.

Acid gases
(e. g. hydrogen bromide, chlorine, hydrogen chloride, hydrogen iodide, phosgene, sulphur dioxide) are fed over a coarse frit into 20% sodium lye, under stirring if possible.

Raney nickel
as an aqueous slurry is mixed with hydrochloric acid under stirring. The solution containing the heavy metal salt is disposed of as Rinsing and washing water containing metal salts. In no case, Raney nickel and filter papers with residues may become dry because this will lead to self-ignition when exposed to air!

Dimethyl and diethyl sulphate
are powerful alkylating reagents. They must be handled in a fume hood; when working with them, protective gloves must be worn to protect the skin from splatters. Disposal is then performed by dripping the reagents into a stirred, concentrated, ice-cooled ammonia solution.

Cyanides (e. g. sodium cyanide, potassium cyanide, hydrogen cyanide)
In aqueous solution at a pH of 10 – 11, all cyanides can be oxidized with a surplus of hydrogen peroxide (H_2O_2) to the the corresponding cyanates. At a pH of 8 – 9, the cyanate is oxidized with additional hydrogen peroxide to form carbon dioxide and nitrogen.

Organic lithium compounds (n-butyl and tertiary butyl lithium)
Destruction of these oxygen-sensitive lithium compounds is achieved by slowly adding isopropanol under inert gas (argon, nitrogen). The isopropanolate is hydrolysed with water, the solution is disposed of as Solvent mixture without halogenated organic solvents.

Sicapent®
Place the desiccant Sicapent® over water into an exsiccator so that it can become completely hydrated. Add the wet Sicapent to water and neutralize with sodium lye. Filter off the carrier material and discard it together with the filter. Pour the aqueous solution into the waste water.

6 Dangers of fire and explosions

This chapter shows how to avoid fire and explosions which may result from chemical work. It answers the following questions:

1. **How to work with flammable liquids, and how their hazard classes are defined**

2. **Which are the spontaneously flammable substances used most frequently in the laboratory, and how they are handled**

3. **What are potentially explosive substances and mixtures, and which classes of substances and mixtures must be assumed to be potentially explosive**

4. **What is to be observed in exothermic reactions**

5. **Which hazards arise from decomposition reactions, and substance classes where the possibility of such reactions must be assumed**

6. **Fire protection devices that need to be present, and things to be observed when using them**

6.1 Flammable liquids

Many liquids used in the laboratory are flammable. In certain concentration ranges which can be learned from tables, their vapours form potentially explosive mixtures with air.

Flammability must be paid attention to when performing chemical reactions, distilling, extracting and storing chemicals, but above all when handling them openly. Here it is to be kept in mind that the density of the gases and vapours is almost always higher than that of air.

Thus, the vapours creep across the benches or the floor and may ignite at completely unforeseen locations.

When bottling and decanting flammable liquids, there is danger of ignition by electrostatic charge. Metal vessels must therefore be grounded.

When flammable liquids are spilled or leaked, even in relatively small amounts, first extinguish all open flames in the vicinity.

If the amounts are larger, the laboratory colleagues must be warned and instructed to leave the room. In case of fire, dispose of the spilled substance only after all fires have been quenched and sufficient aeration provided.

Flammable liquids may be stored at the workplace only in the amounts absolutely indispensable for normal work.

Keep in mind that crammed shelves pose the danger of accidentally throwing down bottles.

Storage

The Ordinance on Hazardous Substances classifies flammable liquids essentially according to their flashpoint and partly according to their boiling point:

The flashpoint is the lowest temperature where under certain experimental conditions the liquid will produce sufficient amounts of vapours so that when mixed with air an ignition source may cause inflammation.

Indication of danger	R phrase	Hazard symbol	Flash point	Boiling point	Example
Extremely flammable	R 12	F^+	< 0 °C	≤ 35 °C	acetaldehyde
Highly flammable	R 11	F	< 21 °C		acetone
Flammable	R 10	none	21 °C ≤ FP ≤ 55 °C		butan-2-ol
None	none	none	(21°C*) 55 °C < FP		cis-decaline

Thus, only flammable liquids with a flashpoint below 21 °C show the flame symbol in the labelling. Some do not comprise any indicator of their flammable properties, i. e. neither flame symbol nor indication of danger (R phrase)! Still the vapours of all flammable liquids can be ignited when the liquid is heated above its flash point (butan-2-ol above 24 °C, superheated oil baths).

Flammable liquids with a flashpoint below 21 °C (highly and extremely flammable liquids; previously liquids of hazard classes AI, AII and B) may be stored at the workplace only for ordinary use in vessels with a nominal volume of no more than 1 l. The number of such vessels is to be limited to the absolutely necessary minimum.

For laboratories where larger amounts of flammable liquids are continuously needed for progress of the work, storage in non-fracture proof containers with a capacity of up to 5 l or in fracture-proof containers with a capacity of up to 10 l an a protected location is permissible.

It is recommended to use rooms or cabinets equipped with aspiration and dyke (e. g. according to DIN EN 14 470-1).

Apart from that, in the laboratory flammable liquids are to be stored in the existing safety cabinets (e. g. according to DIN EN 14 470-1).

(*) In practice it was found that a composition with a flashpoint of no less than 21 °C and no more than 55 °C does not need to be classified as flammable if it does not support combustion in any way and if in handling this composition any hazard can be excluded for everyone. This includes, inter alia, several aqueous mixtures of alcohols serving as disinfectants.

Flammable solvents and reaction solutions may be stored for cooling only in refrigerators whose inside is explosion-proof. Make sure the fridge to be used is marked accordingly.

6.2 Self-igniting substances

Substances which may spontaneously ignite upon contact with air and/or water are another cause for laboratory fires or explosions. In common laboratory practise, these are particularly the alkali metals and their hydrides and white phosphorus.

Raney nickel and a large number of organometallic compounds such as Ziegler-Natta catalysts are likewise dangerous, and their handling requires special working techniques.

Alkali metals react most violently with water, releasing hydrogen, which can lead to oxyhydrogen gas explosions. Potassium (in particular older, encrusted preparations) and sodium-potassium alloys may spontaneously ignite when exposed to air, hence they must be weighed and crushed under an inert solvent (e. g. high-boiling benzine).

Alkali metal fires may be fought only with dry sand or fire class D powder fire extinguishers. Caution: Do not use CO_2 fire extinguishers!

Alkali metals are frequently used for drying solvents, e. g. by pressing sodium wire into the solvent. They may be used only for solvents not reacting with alkali metals (hydrocarbons, ether, tertiary amines). With halogenated hydrocarbons, there is danger of explosive reactions!

In modern laboratory practise, less dangerous drying methods, e. g. use of molecular sieves, should be preferred. Alkali metal residues are disposed of as described in section 5.3.

6.3 Potentially explosive substances and mixtures

The term potentially explosive is used to denote substances or mixtures of substances which may, upon exposure to thermal energy (heat, flames) or mechanical energy (friction, shock), spontaneously react so violently that high release of energy and build-up of high pressure result in very fast propagation of shock waves.

Potential explosives are many organic nitroso and nitro compounds, highly nitrated aromatic compounds, esters of nitric acid, many compounds with N-N bonds (azo and diazo compounds, hydrazoic acid, azides), fulminates, NCl_3, ICl_3 and acetylides, and also many peroxidic compounds (peroxy acids, peroxy esters, peroxides, hydroperoxides).

Mixtures of oxidizing compounds such as nitrates, chlorates, perchlorates, fuming nitric acid, concentrated perchloric acid and solutions of hydrogen peroxide (30 %) with flammable and reducing agents may be potentially explosive. For example, fuming nitric acids reacts explosively with acetone, ether, alcohol, turpentine.

Production of potentially explosive substances as well as their handling requires knowledge of and practical experience with special methods and particular safety measures. Any attempts to produce explosives in the laboratory are most explicitly discouraged! This is forbidden by the provisions of the Explosives Act. You jeopardize yourself and others and will have to face civil and penal consequences for any damage.

Exceptions for research laboratories are regulated by the Explosives Act, which also defines maximum amounts. When working under these exceptional permits, potentially explosive substances and mixtures are to be handled in the smallest amounts possible and only at stations shielded on all sides.

Avoid superheating, vicinity to flames, sparks, shocks, friction and plugging (rigid inclusion).

The reserves of such substances are to be kept as small as possible. They are to be stored at a place safe from flames and heat, in closed containers and away from the work stations, if possible in a separate room.

6.4 Exothermic reactions

Many chemical reactions are exothermic. If the heat produced is not dissipated sufficiently, this leads to self-heating of the reaction mixture and thus to acceleration of the reaction (runaway reaction).

As a consequence, uncontrolled boiling of the solvent, discharge of the reaction mixture from the apparatus or even violent, explosive decomposition reactions may occur.

The danger of a runaway reaction is particularly great if exothermic reactions begin only after an induction period. Examples include production of Grignard compounds or nitration of reactive aromatic compounds. For such reactions, provide an effective cooling bath, and until a controlled reaction is observed, avoid any significant excess of reagent.

Uncontrolled exothermic reactions may also occur during downstream processing, in particular during inactivation of excess reactive reagents such as acid halogenides, alkali metal hydrides etc.

Exothermic reactions are controlled by cooling the reaction vessel or by using reflux condensation.

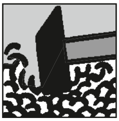
It should be kept in mind here that good mixing favours heat dissipation from the reaction mass, whereas high viscosity or solid precipitations on the cooling area reduce the passage of heat.

Exothermic reactions may also be controlled by slow addition of one of the reaction partners, by adding one of the reaction partners in cooled form or by observation of the sequence of the addition of reaction partners (utilization of thermal capacity). If substances are generated which may react with water, then water must not be used as a coolant.

In the context of exothermic reactions, caution is advised in particular against a significant increase in reaction volume. Switching to a larger apparatus will change the mass of substances and hence the reaction heat in proportion to the third power of the radius of the reaction vessel, whereas the surface of the apparatus which is available for hear dissipation will change only in proportion to the second power of the radius of the reaction vessel.

Thus the danger of self-heating increases continually with increasing mass. Therefore scaling up of the reaction should be performed gradually and under constant supervision for possible exothermic effects.

6.5 Decomposition reactions



Many substances or mixtures prove unstable upon thermal or mechanic stress. Under certain circumstances, they may decompose spontaneously with a high release of energy so that decomposition may take an explosive course.

In laboratory practice, excessive thermal stress may occur during drying or distilling of substances. When drying thermally unstable substances in heating cabinets, select the drying temperature and, if necessary, secure it by an overheating control mechanism so that decomposition cannot be initiated.

As a precautionary measure, distillations should be performed behind protective shields.

During distillation, substances, in particular distillation residues, must never be heated too strongly. If during the course of a distillation process indicators for beginning decomposition should appear (such as sudden foaming, release of gas), a spontaneous course of the decomposition must be expected. If necessary, the danger area is to be cleared and the people in the vicinity are to be warned. The heat source must be removed or switched off from a safe location.

Some substances become mechanically sensitive upon drying (removal of phlegmatization). Examples include diazonium salts and nitrophenolates. When handling such substances, protect them from desiccation.

In laboratory practise, the mechanical and thermal instability of organic peroxides in particular poses a latent danger. Peroxides are formed in many organic solvents during prolonged exposure to air.

Many organic compounds such as diethyl ether, diisopropyl ether, dioxane and tetrahydrofurane, also unsaturated hydrocarbons such as tetraline, cumol, aldehydes, ketones and solutions of these substances tend to form peroxides.

Such peroxides are present only in very low concentrations, but during distillation they accumulate in the residues, and under certain unforeseeable conditions they may cause devastating explosions. The fact that such accidents are rare leads to habituation and hence to inappropriate neglect of the safety precautions described below.

In addition it should be pointed out that peroxides contained in the solvents used will frequently affect purity and yield of the reaction products.

Liquids inclined to form organic peroxides are to be stored in the dark or in bottles of dark glass or opaque material. Prior to distillation or evaporation, they must be examined for presence of peroxides and be cleared of peroxides if required.

Upon receipt or after longer storage, the aforesaid solvents must be tested for peroxides using a peroxide test stick.

Peroxide-containing solvents are purified in accordance with suitable protocols from the literature. New formation of peroxides is prevented by addition of oxidation inhibitors, by storage in dark bottles, but most effectively, in particular for valuable absolute solvents, under inert gas.

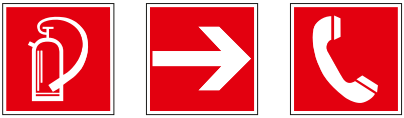
In all chemical syntheses involving peroxides, peroxy acids, hydrogen peroxide, molecular oxygen or ozone, before downstream processing control for the presence of peroxides, which are to be destroyed using a reductive agent if required. Peroxidic compounds as synthesis intermediates should be handled only in diluted solutions.

They should not be isolated in pure form.

6.6 Laboratory fire protection

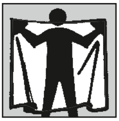
In laboratories, fire blankets and hand-held fire extinguishers are to be provided in easily accessible locations.

Close to the exits, emergency showers are installed. They must be tested once a month for proper functionality.



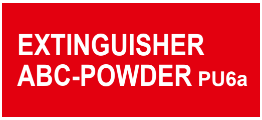
Small fires are to be fought with the existing extinguishing equipment if this can be done without danger.

If the fire is about to expand and get out of control, inform the fire brigade immediately.



Burning clothing must be extinguished under the emergency shower, with fire extinguishers or fire blankets. (Highly volatile solvents often permeate the tissue of the fire blankets and may then ignite again.) If necessary, rolling on the floor, supported by covering with clothes and the like, may extinguish the fire. Burning clothing is to be thrown off as quickly as possible.

In case of major fires of clothing, in particular involving solvents, do not allow burning persons to run away as this will help to spread the fire, but floor them and then extinguish the fire.

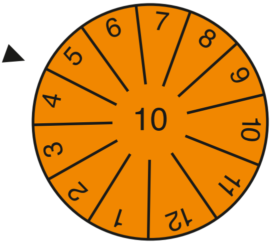


For quenching of laboratory fires, powder extinguishers and carbon dioxide extinguishers are suitable. The latter do not leave residues and may be preferable in the vicinity of valuable measurement devices and the like.

Fires of alkali metals and other reactive metals, metal alkyles, lithium aluminium hydride, silanes and related substances are preferably quenched using extinguishing sand or powder. Under no circumstances may such fires be fought with water! Carbon dioxide extinguishers are likewise unsuitable.

Anybody working in a laboratory should familiarize himself or herself with the type, location and proper usage of the existing extinction equipment prior to beginning work in the lab.

Fire extinguishers must be controlled every two years (seal of approval!).



7 Working with electrical equipment

This chapter describes the dangers arising from incorrect use of electrical devices, and how to avoid them.

7.1 Accidents with electricity

Most accidents with electricity are caused by using damaged or unsuitable electrical equipment or installations. Accidents may also result from incorrect repairs by laymen.

The most important measure is insulation to protect from touching live (i. e. energised) parts.

It is mandatory to observe the following rules:

- When working in the lab, use electrical equipment only in accordance with the operating instructions.
- Equipment and devices must be in impeccable condition.
- The settings of safety devices must not be altered.
- Do not use any wet electrical equipment.
- In case of damage or unusual operating states, switch off the equipment or device and report to an electricity specialist.
- Do not continue to use defective equipment; remove it from usage by others and alert them to the dangers.
- Maintenance and repair work by laymen in the field of electro-technics is not permissible, in particular not on live parts.
- Electrical equipment and devices must comply with the generally recognized rules of technology, in particular the regulations issued by the Society of German Electricians (Verband Deutscher Elektrotechniker e.V., VDE), and must be inspected in regular intervals for proper condition by an electricity specialist or a person skilled in electrotechnics and instructed and supervised by an electricity specialist. These regulations likewise apply to home-made devices.
- For electrical equipment used in laboratories, such as
  - rotary evaporators
  - mobile analysis devices
  - heaters
  - measurement devices
  - mains-operated table lamps
  - stirrers
  - extension and adaptor cables

the inspection intervals regularly amount to 12 months in case of normal operational demands see information «Prüfung ortsveränderlicher elektrischer Betriebsmittel» (BGI/GUV-I 8524).

- Work on electrical devices and equipment may be performed only by electricity specialists.

Electricity specialists are defined by the accident prevention regulation

«Elektrische Anlagen und Betriebsmittel» (BGV/GUV-V A3) as follows:

The term **electricity specialist** denotes a person who is capable, by virtue of his/her vocational training, knowledge and experience as well as knowledge of the relevant regulations, to judge the tasks entrusted to him/her and to detect potential dangers.

7.2 Physiological effects of electric currents

If a person gets into an electric circuit, his/her body acts as a resistor. Ohm's Law is applicable: $U = R \times I$.

The electric resistance of the human body can be assumed to amount to approximately $R = 1000\ \Omega$, resulting in the possibility of dangerous currents even at low voltage:
At a nominal voltage of 230 V, a current of 230 mA can flow through the body.

Studies have shown that for 50 Hz AC the maximum which can be tolerated by human beings is a current of $I = 25$ mA.

DC and AC of higher frequency result in slightly more favourable values. However, even brief shocks of lower current intensity may lead to secondary accidents, e. g. falling from a ladder.

With regard to the physiological effects of a current through the body, we may discriminate the following four ranges:

Range I (0 – 25 mA)

Slight increase in blood pressure, above 10 mA muscle spasms, sticking (let-go limit) to the live part, after longer periods spasms of the respiratory muscles.
▶ Generally not lethal.

Range II (25 – 80 mA)

If the circuit includes the heart, cardiac arrest and respiratory paralysis due to muscle spasms may result; after 30 sec, ventricular fibrillation is possible, and oxygen transport to the tissues is blocked.
▶ Circulatory failure may lead to death.

Range III (80 – 5000 mA)

Severe increase in blood pressure, spasms of the respiratory muscles, high probability for ventricular fibrillation after exposition to the current as short as 0.3 sec.

Range IV (> 5000 mA)

Frequently, spontaneous cardiac arrest occurs during exposition to the current, often no ventricular fibrillation, but thermal effects of electricity (burns by electric arc). Currents of these dimensions generally occur in high-voltage accidents. In addition to the electrical flow-through, there may be external burns.
▶ Death often only after days or weeks.

8 Working with radiation

This chapter provides rules for handling radioactive material. It answers the questions:

⚠ **How to protect from external and internal irradiation.**

⚠ **How to avoid contamination.**

Furthermore it provides information for working safely with X-rays and with intense light sources.

8.1 Working with radioactivity

According to § 3 of the Ordinance on Prevention of Damage by Ionising Radiation, a.k.a. Radiation Protection Ordinance (Verordnung über den Schutz vor Schäden durch ionisierende Strahlung or Strahlenschutzverordnung, July 20th, 2001), handling of radioactive substances includes preparation, production, storage, processing, other uses and disposal of radioactive substances, so that laboratory work is also covered by the scope of this ordinance.
If any work relating to radioactive substances is to be performed which exceeds the extent of the activities not requiring authorisation as listed in Annex I to the Radiation Protection Ordinance, the competent authorities are to be notified, and the work must not be performed before authorisation has been granted. Activities not requiring authorisation include work with radioactive substances below certain permitted limits.

8.1.1 Rules for handling radioactive substances

When working with radioactive substances, dangers for the laboratory staff may result from the possibility of

- external irradiation,
- incorporation of radioactive substances and thus danger by internal irradiation,
- contamination e.g. of the skin. Contamination results in external irradiation with a radiation source: body distance of zero. There may, however, also be the danger of resorption of radioactive substances through the skin into the body.

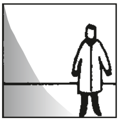
These dangers can be avoided or at least minimized by instructing the laboratory staff in accordance with § 38 of the Radiation Protection Ordinance before handling any radioactive materials. Instruction is to be performed on the basis of the radiation protection directive to be produced in accordance with § 34 of the Radiation Protection Ordinance.

The radiation protection directive and instruction must comprise and relate to the relevant contents of the Radiation Protection Ordinance and the notice of approval, as well as guidelines and norms. In any case, they must take into account the specific dangers of the individual radioactive substance to be handled (physical and chemical properties and type of radiation: α, β and/or γ rays).

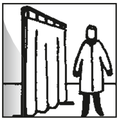
Thus, only general provisions for working safely can be described here. These are:

8.1.2 Protection from external irradiation

1. Protection from external irradiation when working with γ-emitting nuclides

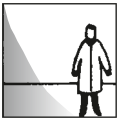


Keep your distance!
The dose rate decreases in proportion to the square of the distance from the radiation source (and in addition, linear to the activity of the source).



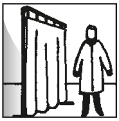
Shielding measures
can be implemented e. g. with mobile lead walls or lead building blocks enclosing the radiation source. The required thickness of the lead depends on the activity and energy of the γ emitters and on the (inevitable) exposition time of the lab staff.

2. Protection from external irradiation when working with β-emitting nuclides



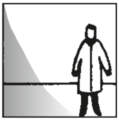
Keep your distance!
This applies in particular to nuclides with energies in excess of 200 keV. The dose rate decreases in proportion to the square of the distance from the radiation source, but in contrast to γ radiation with an additional weakening factor of β rays in air which is proportional to the distance selected.

When working with high-activity sources of high-energy β ray emitters, remote handling devices may be used.



Shielding measures
can be implemented with materials of low density. Because of the higher degree of attenuation of β radiation compared to γ radiation, glass or plastic panes are often sufficient as shielding materials. However, ample thickness of the shielding materials and selection of appropriate materials are required to minimize the hazard posed by bremsstrahlung (X-ray radiation – do not use lead!)

3. Protection from external irradiation when working with α-emitting nuclides



Keep your distance!
Due to the lower range and significant weakening of α radiation in air, keeping one's distance is not as important as with γ and β emitters. However, the distance must not be allowed to become so small that contamination e. g. of the skin may occur.

Shielding measures
In general, plastic or glass vessels with low wall thickness will be sufficient. Lead shielding only for α-emitting nuclides with concomitant γ emission.

8.1.3 Protection from internal irradiation (incorporation of radionuclides)

Protection from internal irradiation, i. e. avoidance of incorporation of radionuclides, is of particular importance when working with α emitters.

α rays, but also other corpuscular rays of comparable mass, do effect the highest damage on the body when compared to γ and β rays of the same energy.

Hence, beginning at approximately 100× the permitted limit α emitters should, if there is any danger of release, be handled in glove-boxes.

Eating, drinking, smoking, snuffing and the use of cosmetics are forbidden in the control area, lest radioactive substances should enter the body via mouth or nose.

Use of mouth-operated pipettes is absolutely prohibited.

In order to avoid inhalation of airborne radioactive substances, these should be handled in fume hoods or in aspirated glove-boxes, depending on the degree of release.

Work with appropriate retention devices (receivers, cryotraps) to minimize the risk of release.

The technical ventilation in the control area must be of a dimension sufficient to ensure that the concentration of radioactive substances in the laboratory air will not become too high.

Optical and acoustical monitoring units must be installed to control the ventilation system.

8.1.4 Protection from contamination

The laboratory staff and students will have to pay particular attention to protection from contamination. The values for contamination of skin and other organs according to §§ 54, 55 of the Radiation Protection Ordinance must be observed. That is to say that even the lowest detectable contamination of the skin and other organs is to be avoided at any rate.

Working surfaces and equipment are to be secured against contamination and hence spreading of potential contamination to the body by covering with foils and laying with absorbents.

In the control area, always wear personal protective equipment (protective coat, protective suit, protective gloves, overshoes and the like). Do not take off this protective equipment in the lab.

All incidents, such as ventilation failure or breakdown of measuring devices, which might affect working safety, must be reported to the radiation protection officer. Keep the laboratory doors closed (maintenance of negative pressure).

In order to avoid contamination, do not take any personal belongings (e. g. handbags) with you into the control area. Between the individual operations and in particular before leaving the control area, check hands, feet and other protective equipment for contamination. Report any detected contamination immediately to the radiation protection officer.

Objects may leave radiation protection areas (control and monitoring areas) only if they do not exceed the limits as specified in Annex III, Column 4 (§ 44 Radiation Protection Ordinance). The laboratory clothing is to be taken off in a black-and-white area and to be replaced with streetwear.

In contrast to the protective measures only generally touched here, the radiation protection directive to be produced in accordance with § 34 of the Radiation Protection Ordinance must comprise detailed provisions relating to the individual laboratory procedures.

§ 95 I and XII of the Radiation Protection Ordinance in combination with Annex XI, part B regulates work with natural radioactive substances in the workplace (uranium and thorium compounds for chemical-analytical or chemical-preparative purposes – this does not affect radioactivity).

8.2 Working with X-rays

Like nuclear γ ray sources, X-ray machines are among the sources of danger frequently met in chemical laboratories. Rooms where such machines are installed are labelled with danger signs and may be entered by authorized staff only.

Their operation is permitted only after notification of and, if required, authorisation by the authorities.

Before working with X-ray machines (X-ray ultrastructure devices, X-ray fluorescence spectroscopes, Mößbauer spectrometers), each student must have been instructed by the competent radiation protection officer.

Students may participate in operating an X ray machine or a source of stray radiation only in the presence and under the supervision of the radiation protection officer in charge (§ 13 IV Ordinance on X-Rays, Röntgenverordnung).

A film dosimeter, which is to be officially evaluated in regular intervals, must always be worn while in rooms with γ ray sources.

8.3 Working with powerful sources of light

Powerful sources of light such as lasers, but also high-pressure lamps (xenon, mercury) and arc lamps are sources of danger. In laboratories where high-pressure or arc lamps are active, goggles with a strong UV filter must be worn. Good ventilation of the rooms is required because of potential development of ozone.

The eye is already endangered by laser radiation of very low energy density. However, high energy density jeopardizes the skin as well and potentially also the organs below. Guidelines for the highest permissible irradiation intensities (MZB-Werte) can be found in the Accident Prevention Regulation «Laserstrahlung» (BGV/GUV-V B2).

Laser areas must be delimited and marked during laser operations. At the accesses to laser areas, laser operations are to be indicated by warning lights.

Only employees who have been instructed with regard to the dangerous effects of laser radiation and the necessary protective measures may enter the laser area. They must be protected from the effects of laser rations by suitable measures; in particular, they must use suitable eye protection.

Lasers may be operated by instructed staff only. When operating high-powered lasers of classes 3R, 3B and 4, which pose a significant danger potential, a laser protection officer is responsible for safe operations of the laser devices.

9 Health hazards

This chapters describes the health hazards which hazardous substances present. The course of intoxications and typical symptoms thereof are discussed. Classification is performed according to possible damage to certain organs or organ systems as well as to similarity of effects. A separate section deals with protective measures for work with carcinogenic and mutagenic substances. The chapter additionally comprises a list of the most important carcinogenic substance classes and, in Annex A, a list of substances classified as carcinogenic, mutagenic and toxic for reproduction.

9.1 General toxicology of chemical materials

Hazardous materials may affect the health of the human body due to their acute and chronic toxicity as well as their corrosive, irritant, sensitizing, carcinogenic, mutagenic and reproduction-related toxic properties. All these factors are considered in the classification and labelling of a substance. § 5 of the Ordinance on Hazardous Substances and the EU guidelines referred to therein comprise extensive regulations relating to the criteria according to which a substance is to be classified and labelled.

The LD_{50} value (LD: lethal dosage), determined in animal tests, is an important parameter for assessment of the acute toxicity of a substance. The LD_{50} value describes the dosage – in mg of substance per kg of body weight –, after whose administration 50 % of the experimental animals die within 14 days. Depending on the experimental conditions, LD_{50} oral after uptake via the gastrointestinal tract must be discriminated from LD_{50} dermal after uptake through the skin. In addition to the LD_{50} lethal dosage, a lethal concentration LC_{50} inhalative is used for description of the acute toxicity of a substance. LC_{50} inhalative is that aerial concentration in mg substance per l of air which causes death of 50 % of the experimental animals within 14 days after four hours of exposition.

According to the applicable EU guideline, a hazardous substance is classified with regard to acute toxicity according to the following criteria:

very toxic

LD_{50} oral, rat: ≤ 25 mg/kg
LD_{50} dermal, rat or rabbit: ≤ 50 mg/kg
LC_{50} inhalative, rat, for aerosols/dusts: ≤ 0.25 mg/l
LC_{50} inhalative, rat, for gases/vapours: ≤ 0.50 mg/l

Examples include: Hydrogen sulphide, hydrogen cyanide, dimethyl sulphate, phosgene, nitrobenzene and acrolein.

toxic

LD_{50} oral, rat:
$25 \text{ mg/kg} < LD50 \leq 200 \text{ mg/kg}$
LD_{50} dermal, rat or rabbit:
$50 \text{ mg/kg} < LD50 \leq 400 \text{ mg/kg}$
LC_{50} inhalative, rat, for aerosols/dusts:
$0.25 \text{ mg/l} < LC50 \leq 1 \text{ mg/l}$
LC_{50} inhalative, rat, for gases/vapours:
$0.50 \text{ mg/l} < LC50 \leq 2 \text{ mg/l}$

Examples include: carbon disulphide, methanol, acetonitrile, benzene, phenol, carbon tetrachloride and chlorine.

harmful

LD_{50} oral, rat:
$200 \text{ mg/kg} < LD50 \leq 2000 \text{ mg/kg}$
LD_{50} dermal, rat or rabbit:
$400 \text{ mg/kg} < LD50 \leq 2000 \text{ mg/kg}$
LC_{50} inhalative, rat, for aerosols/dusts:
$1 \text{ mg/l} < LC50 \leq 5 \text{ mg/l}$
LC_{50} inhalative, rat, for gases/vapours:
$2 \text{ mg/l} < LC50 \leq 20 \text{ mg/l}$

Examples include: toluene, xylene, pyridine, n-hexane, nitromethane, chloroform and iodine.

9.1.1 Course of intoxications

The course of intoxications may be fulminant or delayed (acute or chronic poisoning). However, these terms are also used to discriminate between one-time and long-term exposition to noxious substances. In general, high single doses or concentrations result in acute poisoning, whereas chronic poisoning is caused by repeated low doses, each of which individually has only a weakly toxic effect.

The latency between the time of exposition and the onset of detectable health damage may vary widely (from seconds to decades). Chronic intoxication may be based on accumulation of the noxious substance in the organism (as, e. g., in chronic heavy metal poisoning).

An important concept is the half-life of a foreign substance in the organism. This value indicates the time after which one-half of the ingested dose is removed from the body again. However, chronic exposition to low doses may lead to damage even without accumulation. In this case, the effects of the individual doses are additive (cumulation of effects).

The dosage of a hazardous substance below which there no toxic effect can be detected, even after long-term exposition, is called the threshold value. The existence of threshold values may be explained by two different mechanisms:

Firstly, elimination may be swifter than uptake; secondly, cellular damage may be repaired more quickly than it is done.

9.2 Fate of noxious substances in the organism

For assessment of the toxic effects of a compound, which in most of the cases will depend on the concentration of the substance at the effective site, it is necessary to know the fate of the substance in the organism.

The interaction between the toxic substance and the organism can be divided into the following phases:

- ▶ Exposition and uptake,
- ▶ distribution in the organism,
- ▶ conversion (metabolism) of the absorbed substance and
- ▶ elimination of the substance.

9.2.1 Exposition and routes of uptake

As a rule of thumb, health impairment is determined by the product of toxicity and absorbed dose. Absorption can occur

- ▶ inhalatively via the lungs (respiratory toxins),
- ▶ orally via the gastrointestinal tract,
- ▶ dermally via skin and mucosal membranes.

Inhalation is the most important form of exposition by which toxic substances may enter the body. Oral incorporation and resorption through the skin are easier to avoid.

9.2.2 Distribution in the organism

Local effects arising at the point of exposition are to be discriminated from resorptive effects based on the substances being distributed in the body and reaching the affected organs.

The local effects such as chemical burning of the skin or mucosa by acids or lyes are, once they have occurred, irreversible. By contrast, resorptive effects are usually reversible, provided that countermeasures have been initiated early enough.

From the blood, substances are absorbed into the organs by a variety of mechanisms. Uncharged molecules can diffuse through the cell membrane, other molecules use physiological carriers.

Chlorinated hydrocarbons with narcotic effects enter the brain by diffusion.

High lipid solubility increases uptake and decreases elimination from lipid-rich tissues.

Accumulation of mercury, by contrast, is a metabolism-dependent transport.

The liver and kidney have a high capacity for accumulation of toxic substances. They are also the most important organs for conversion and excretion of the compounds.

9.2.3 Metabolism

The majority of organic compounds are not excreted unchanged. They are chemically modified by attacks of cellular enzymes. In the liver, absorbed chemicals, drugs and noxious substances may be oxidized, hydrolysed, reduced and conjugated to sulphuric or glucuronic acid. In general, these metabolic reactions result in compounds which can be excreted more easily (detoxification).

However, metabolic conversion may also lead to compounds which are more toxic than the original substances. In contrast to detoxification, this is called physiologic toxification. Aniline, for example, is oxidized to phenyl hydroxyl amine, whose further conversion to nitrosobenzene leads to the formation of methaemoglobin.

Carbon sulphide reacts with the amino groups of peptides to form dithiocarbamates which bind metals by complex formation and interfere with trace element metabolism.

Carbon tetrachloride produces reactive free radicals which are at least partially responsible for the hepatotoxic effect.

The degradation of methanol leads, via formaldehyde formation, to production of formic acid which ultimately results in blindness.

The insecticide parathion (E 605) acts as an acetylcholine esterase inhibitor; this effect is increased by oxidation to paraoxon.

9.2.4 Elimination

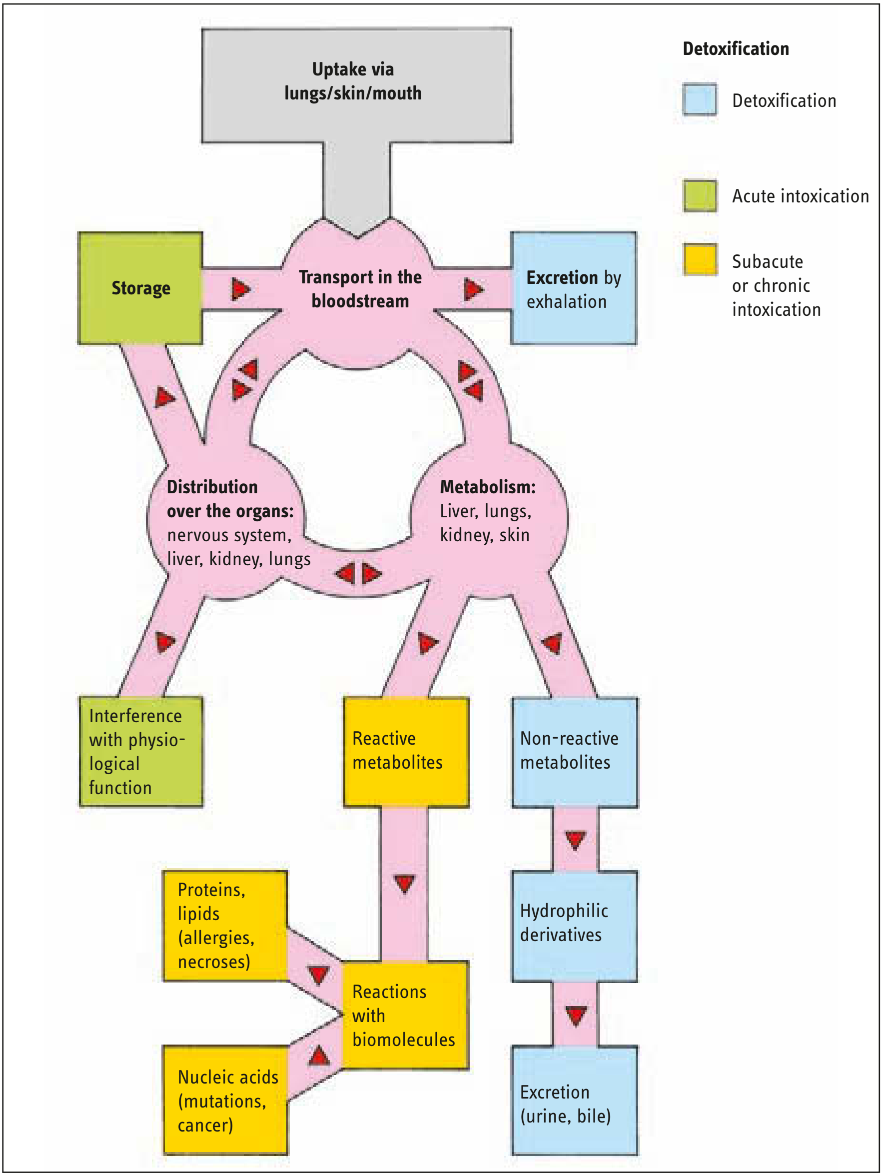
The term elimination denotes metabolic removal of a toxic substance from the body, storage in the form of indifferent substances and excretion. The main excretory routes are exhalation, urine and faeces.

Generally it may be said that all substances which are inhaled in the form of vapours or gases can be eliminated by exhalation. Most other toxic chemicals and their metabolites are excreted via urine or faeces.

For intestinal excretion, the liver is the most important source. Excretion through the kidneys depends on the filtratability of the substance and the ability of the tubular cells to accumulate or to secrete the substance.

Complexing agents may increase excretion if they compete with proteins for binding of the substance. Thus, excretion of of heavy metals can be improved by administration of complexing agents, e. g. excretion of inorganic mercury by BAL (British Anti-Lewisit, 2,3-dimercapto-1-propanol) or of lead by EDTA (ethylene diamino tetraacetate).

The schematic representation of the fate of a toxic substance in metabolism gives an overview of the various possibilities of intoxication and detoxification upon entry of a toxic, hydrophobic substance into the organism (see picture 20).


Uptake via lungs/skin/mouth
Storage
Transport in the bloodstream
Excretion by exhalation
Distribution over the organs: nervous system, liver, kidney, lungs
Metabolism: Liver, lungs, kidney, skin
Interference with physiological function
Reactive metabolites
Non-reactive metabolites
Proteins, lipids (allergies, necroses)
Reactions with biomolecules
Hydrophilic derivatives
Nucleic acids (mutations, cancer)
Excretion (urine, bile)
Detoxification
Detoxification
Acute intoxication
Subacute or chronic intoxication

Picture 20

9.3 Effects of noxious substances

Corrosive and irritant gases irritate the skin and mucosa, in particular of the airways and the eyes. Their presence is therefore felt by an urge to cough, burning in nose, throat and eyes and lacrimation.

However, with certain gases the first signs of intoxication may be very slight, but nevertheless several hours later severe and potentially lethal damage to the lung may result (pulmonary oedema). For example, a few breaths of nitric oxides are sufficient to induce pulmonary oedema.

9.3.1 Corrosive and irritant gases

Hydrogen chloride and hydrogen fluoride are strong irritants affecting the upper airways and the eyes, where they can lead to conjunctivitis and damage to the cornea.

The colourless *sulphur dioxide* is characterized by its pungent odour. It irritates the mucosal membranes; in higher concentrations, it causes difficulties of breathing, potentially pneumonia and impairment of consciousness.

Chlorine and *bromine* vapours are significantly heavier than air and accumulate close to the floor where they may remain for extended periods of time. If inhaled, they cause coughing, difficulties of breathing and asphyxiation.

Higher concentrations of *ammonia* may likewise cause asphyxiation and, after rapid loss of consciousness, death.

Formaldehyde causes dermal allergies and shows a remarkably strong irritant effect on the mucosal membranes of the eyes and upper airways.

As particularly strong ocular irritants, *chloroacetone and bromoacetone, bromoacetate ethyl ester and acrolein* deserve special mentioning. Even minimum concentrations in air cause strong burning in the eyes, lacrimation and blepharospasms. Only higher concentrations harm the airways and skin.

Phosgene, a colourless gas with a slight odour of rotting fruits, is used in large amounts as an intermediate in chemical syntheses, but is also generated during thermal decomposition of chloro- and fluorohydrocarbons. Low concentrations induce urge to cough, anxiety and nausea. In severe cases, pulmonary oedema and cardiac insufficiency may result even several hours later, often with fatal results.

Ethylene oxide irritates the mucous membranes and causes headache, vomiting and difficulty of breathing. *Ethylene* imine vapours cause severe irritations of the eyes and airways, in severe cases pneumonia and pulmonary oedema.

9.3.2 Gases as haematotoxins, cytotoxins and neurotoxins

In pure form, *carbon monoxide* is colour- and tasteless and hence not self-alarming. It has an affinity to the blood pigment haemoglobin which is approximately three hundred times higher than that of oxygen, and thereby it disrupts the body's oxygen supply. It causes the frequent cases of gas poisoning by smouldering fire. Longer exposition to concentrations as low as 0.01% (v/v) cause headache; above 0.2% (v/v), deep stupor, decreased heart rate and finally death may result.

Hydrogen sulphide, whose characteristic odour is not perceptible at higher concentrations, is a strong neurotoxin. It irritates the airways; higher concentrations may lead to sudden loss of consciousness and finally death by respiratory paralysis.

Hydrogen cyanide (prussic acid) is easily released from its salts by acids. In can be absorbed into the body not only via the airways but also through the skin. It blocks cellular respiration by inhibition of enzymes. Even very small amounts (about 1 mg/kg of body weight) may be fatal.

Finally *arsine*, reeking of garlic, and *phosphine* should also be mentioned as extremely toxic and dangerous gases.

9.3.3 Asphyxiating gases

In laboratory practice, *gaseous nitrogen* is primarily used as inert gas, *liquid nitrogen* as cryogenic agent. There is no way to discriminate by sensory perception from normal air an atmosphere wherein addition of nitrogen has reduced the oxygen content to less than the normal concentration. When inhaling such an atmosphere, however, the organism, in particular the sensitive brain, is no longer sufficiently supplied with oxygen. If the oxygen concentration drops below 12 % (v/v), there is acute danger to life; at concentrations from 12 to 15 % (v/v), at least performance is impaired. One breath of pure nitrogen is sufficient to lead, without any premonition, to loss of consciousness and respiratory arrest, leading to death in case reanimation is not begun in due time.

Argon, which is also used as an inert gas, has the same effect. Being heavier than air, it accumulates in depressions.

Other gases such as *methane, propane* and *butane* may also cause asphyxiation by displacement of atmospheric oxygen.

Due to its high density, *carbon dioxide*, used as a cryogenic agent and inert gas, will also accumulate in depressions and basement rooms. However, this gas also has a specific toxic effect. Beginning with 5 % (v/v) CO2 headache and vertigo may occur, at 15 % (v/v) unconsciousness and death, even if there are still sufficient amounts of oxygen present.

9.3.4 Acids and lyes

Concentrated acids and *lyes* (nitric acid, hydrochloric acid, sulphuric acid, sulphur trioxide, formic acid, soda lye, lime potash and others) cause chemical burns of the skin and mucous membranes, which may range, depending on the concentration of the substances and the duration of exposition, from superficial irritation to extensive destruction of the skin and the tissues below. Eyes and airways are at particular risk.

Lyes frequently do worse harm than acids, since lye burns heal only slowly. Even a few drops of potassium or calcium hydroxide solutions may lead to blindness.

Injuries caused by *hydrofluoric acid* are also extremely dangerous since pain often does not begin after a few hours after exposition. Quick and specific medical care is of particular importance after contact with hydrofluoric acid.

If work must be performed during which squirting of acids or lyes must be expected, the eyes must be protected by tight-fitting closed goggles, if necessary in combination with a face shield.

Gloves of nitrile or butyl rubber or PVC may be used for hand protection.

Depending on the degree of potential danger, in addition aprons and boots of suitable materials (PVC, rubber) must be worn.

9.3.5 Solvents

Upon inhalation, almost all *solvents*, even those without specific toxic effects, such as diethyl ether, acetone, ethyl acetate, have intoxicant and in higher concentrations (several % v/v) narcotic effects. Longer exposition to higher concentrations presents danger of death by respiratory paralysis.

Chlorohydrocarbons such as monochloromethane, dichloromethane, carbon tetrachloride and trichloroethylene may additionally cause liver and kidney damage and circulatory disturbances.

Because of their high acute toxicity, dichloromethane *(methylene chloride), chloroform* and *carbon tetrachloride* must not be used for cleaning and degreasing e. g. of glass equipment. Inhalation of low amounts of chlorohydrocarbons, including amounts below the olfactory threshold, for a longer period of time may cause chronic health problems such as liver damage. This toxicity is increased by alcohol and certain drugs (e. g. barbiturates).

9.3.6 Dusts

Inhaled *dusts* act as foreign bodies and will therefore always lead to irritation of the lungs and airways.

The biodegradation-resistant minerals *quartz* and *asbestos* have been found to be particularly dangerous in this respect. Upon chronic exposition, they may cause severe lung disease if the dusts are present in sufficiently fine-grained form to enter the lungs together with the inhaled air (respirability).

Inhalation of *quartz dust* with an aerodynamic particle diameter of less then 10 µm (alveolar fraction) may result in the condition known as silicosis within 5–10 years, sometimes earlier. Bronchitis, difficulty of breathing and cardiac insufficiency may result and, in the worst case, be fatal. Things may be worsened by tuberculosis as a complication.

The various naturally occurring *asbestos minerals (chrysotile asbestos, amphibolic asbestos)* are present in the form of fibres and have a propensity for splitting up, parallel to the fibre axis, into minute microfibres. If the fibre diameter falls below 3 µm, fibres with a length of up to 100 µm may be deposited in the lungs by inhalation. Thence they may move on to other tissues, in particular to the pleura (pleural drift). In the lungs, asbestos fibres may cause asbestosis, a condition similar to silicosis and usually preceded by massive exposition. Moreover, after a latency period of 20 years or more, even after low-degree exposition asbestos fibres may cause pulmonary cancer and carcinomas of the peritoneum and pleura (mesotheliomas).

9.3.7 Workplace limit values

For prevention of the toxic effects of substances which may be taken up via the airways it is important to know the concentrations in the workplace atmosphere which do not, according to the opinion of experts in toxicology and workplace medicine, pose any danger to health, even after prolonged exposition. These are the workplace limit values (WLVs) (Arbeitsplatzgrenzwerte).

The following table gives some examples of workplace limit values.

As of February 2009

Example	ml/m³ (ppm)	mg/m³
mercury		0.1
phosphine	0.1	0.14
nitric acid	1	2.6
hydrogen chloride	2	3
fluorine	1	1.6
chlorine	0,5	1,5
N,N-dimethylformamide	10	30
diethyl ether	400	1200
dioxane	20	73
acetone	500	1200
ethanol	500	960
methanol	200	270
toluene	50	190
tetrahydrofurane	50	150
pentane	1000	3000
cyclohexane	200	700
n-hexane	50	180
acetonitrile	20	34
carbon tetrachloride	0.5	3.2
carbon monoxide	30	35
carbon dioxide	5000	9100

from: TRGS 900 «Workplace Limit Values» (Arbeitsplatzgrenzwerte), January 2006 issue as updated in February 2009.

The WLV is the maximum allowable value for the average concentration of a substance in the workplace atmosphere, weighed by time and with regard to a given reference time span. It indicates the concentration of the substance for which acute or chronic detrimental effects on health are generally not to be expected.

WLVs are defined for healthy persons of working age. The WLVs have replaced the former Maximum Workplace Values (MWVs) and Workplace Exposure Limits (WEL values). This became necessary because some MWVs and, by definition, all WELs were not based on occupational medicine but on technical considerations. The WLVs are defined – after a vote by the Committee for Hazardous Substances (CHS), an expert panel representing the groups relevant in the field of hazardous substances – by the German Federal Ministry for Labour and Social Affairs in the TRGS 900 «Workplace Limit Values» (Arbeitsplatzgrenzwerte) and are thus legally binding.

9.4 Cancerogenic, mutagenic and reproduction-toxic substances

9.4.1 Legal basis

Handling of cancerogenic, mutagenic (i. e. affecting the genetic material) and reproduction-toxic substances (so-called CMR substances) requires special care. These substances may cause irreversible and cumulative health damage even in very low dosages. *Mutagenic substances* may, by damaging the genetic material of the germ cells, produce inheritable genetic damage; *cancerogenic substances* may, by doing the same to the genetic material of somatic cells, induce tumours. Cancerogenic substances are peculiar in that there is generally a long time of latency (years or decades) between exposition and the onset of cancer.

Substances affecting reproduction can be divided into embryotoxic/foetotoxic substances on the one hand, which cause non-inheritable harm (abnormalities, deformations) to the embryo/foetus, and substances affecting male or female fertility in the other.

Because of the special dangers from cancerogenic, mutagenic and reproduction-toxic substances, attention is to be paid to bans on production and use (§ 18 in combination with Annex IV to the Ordinance on Hazardous Substances and the Chemicals Prohibition Ordinance [Chemikalienverbotsverordnung]), to employment prohibitions and limitations (Protection of Expectant and Nursing Mothers Act [Mutterschutzgesetz], Ordinance on Guidelines for the Protection of Expectant and Nursing Mothers [Mutterschutzrichtlinienverordnung] and the Youth Employment Protection Act [Jugendarbeitsschutzgesetz]) as well as to special protective measures (§ 11 of the Ordinance on Hazardous Substances) and obligations to information (§ 14 of the Ordinance on Hazardous Substances).

For expectant mothers, the Ordinance on Protection of Mothers at the Workplace (Verordnung zum Schutz der Mütter am Arbeitsplatz, Art. 1 of the Ordinance on Guidelines for the Protection of Expectant and Nursing Mothers) prescribes a general ban on exposition to cancerogenic, mutagenic or embryotoxic/foetotoxic substances.

A register of the substances which must be classified, according to assured and verified scientific findings, as cancerogenic, mutagenic or reproduction-toxic, is found in Annex A.

For many toxic substances, dosage-effect relations allow to list a threshold value (NOEL = No Observed Effect Level) below which, in consideration of the test conditions, no detectable effects (damage) are observed. For these substances, WLVs can be defined which will generally correspond to the threshold values.

For cancerogenic or mutagenic substances, on the contrary, it will generally not be possible to define threshold values.

It is to be assumed that even minimal exposition to such substances which may cause damage to the genetic material, the DNA, may result in irreversible damage.

9.4.2 Important classes of cancerogenic substances and of substances suspected to be cancerogenic

1. **Alklyating compounds**, e. g. dimethyl sulphate, methyl iodide, diazomethane, epichlorhydrine, bis(chlormethyl) ether, ethylenoxide, ethylenimine, vinylchloride.
2. **Polycyclic aromatic hydrocarbons and heterocycles**, e. g.benz[a]anthracene, dibenz[a,h]anthracene, benzofluoranthrenes, benzo[a]pyrene, 2,3,7,8-tetrachlordibenzo-p-dioxine.
3. **Aromatic amines**, e. g. o-phenylendiamine, 2-naphthylamine, benzidine and certain 3,3'-disubstituted benzidines, 4-aminobiphenyl.
4. **Aromatic nitro compounds**, e. g. 2-nitronaphthalene, 4-nitrobiphenyl.
5. **N-nitroso compounds**, e. g. nitrosamines (N-nitrosodiethylamine, N-nitrosopyrrolidine), nitrosamides (N-nitroso-N-methyl-urea).
6. **Azo compounds and hydrazines**, e. g. diazomethane, 4-aminoazobenzene, azo dyes with a cancerogenic amino component, hydrazobenzene, hydrazine and its dialkylated derivatives.
7. **Heavy metals and their compounds**, e. g. cadmium or cobalt dusts and their compounds, nickel dusts, nickel sulphide, nickel oxide and chromium(VI) compounds.
8. **Fibre dusts**, e. g. asbestos, erionite, ceramics fibres made of aluminium oxide, potassium titanate or silicium carbide.

9.4.3 Biochemical effects of cancerogenic substances

Cancerogenic substances (carcinogenes) directly or indirectly interfere with cellular metabolism, turning normal cells into tumour cells. Local neoplasms at the site of exposition may form as well as malign tumours in other tissues or target organs at a distance from the site of primary exposition (bladder tumour caused by benzidine, mesothelioma after exposition to asbestos, pronounced organotropy of dialkyl nitrosamines).

The *partial doses* of a cancerogenic substance accumulate in their cancerogenic potential. In animal experiments, tumour probability increases and latency time decreases with increasing total dosage.

The effects of different carcinogens may be additive or hyperadditive (potentiating). The term *cocarcinogene* is used to denote substances which alone do not induce malignant transformation of cells but enhance the effects of carcinogenic substances. As a general mechanism of action of organic carcinogens of different structures, alkylating or arylating reactions with cellular macromolecules (nucleic acids, proteins) were identified.

Some compounds have alkylating effects without enzymatic activation (direct alkylants), such as dimethyl sulphate and diazo methane; others become active only by being converted, by cellular metabolism, to reactive intermediates (indirect alkylants), such as dimethyl nitrosamine.

Aromatic hydrocarbons are metabolically oxidized to form polar compounds (inter alia degradation to aromatic alcohols), which are rendered capable of being excreted in particular by conjugation with sulphuric acid and glucuronic acid. However, the pathway of metabolic detoxification comprises reactive intermediates (epoxides), which in turn may react with desoxyribonucleic acids. In this case, the inert starting compounds are referred as as *precarcinogens*, which are converted into *ultimate carcinogens* by enzyme-catalysed reactions.

Among the class of polycyclic hydrocarbons, some are precarcinogens, others are not. Thus, without detailed studies no statements can be made regarding the hazardousness of any particular substance. Consequently, precautionary measures must include all substances as long as their harmlessness has not been proven.

As there are interindividual differences in metabolism and the enzymes involved may be induced, by drugs or chronic exposition to noxious substances, to different degrees, the danger to different individual upon exposition is not equally great.

9.4.4 Safety measures for handling cancerogenic and mutagenic substances

Obligation to substitute and to minimize
The prime requirement according to the Ordinance on Hazardous Substances is to replace hazardous substances with less dangerous ones or to change over, respectively, to procedures avoiding or minimizing particular dangerous starting substances or intermediates. For example, in many cases benzene as a solvent may be replaced with toluene or cyclohexane, or N-nitroso-N-methyl-urea for the synthesis of diazomethane with the less dangerous N-nitroso-N-methyl-p-toluenesulphonamide.

If a possible substitution is rejected, the reasons for this must be stated in the documentation of the danger assessment. In this case, special measures are required:

Special protective measures

- Perform any work with CMR substances in a fume hood using the smallest amounts possible and closed equipment if feasible.

- Avoid direct skin contact at any rate. Provide and wear suitable personal protective equipment (protective gloves, if required further personal protection and respiratory protection).

- Make sure that no persons foreign to the laboratory or course enter rooms where CMR substances (or other dangerous toxic substances) are handled. In cases where work on CMR substances of category 1 or 2 (in humans or animals models, respectively, demonstrated to be dangerous) is performed, delimit and mark the areas for handling. This may be, e. g., a single hood.

Disposal measures
After use, pretreat all contaminated flasks, pipettes, spatulae etc. chemically in such a way that the cancerogenic and mutagenic compounds are converted into less noxious substances. Example: Reaction of dimethyl sulphate with ammonia solution.

Collect cancerogenic and mutagenic substances in separate waste containers. The filling of these containers must be done in hoods or under aspiration. The containers are to be kept closed.

Convert spilled substances, if possible, to less noxious ones; absorb liquids with suitable absorbent granulates, package these into tight plastic bags and have them burned properly. When disposing of spilled substances, use personal and respiratory protection!

10 Respiratory protection

10.1 Physiological basis of respiration

Breathing is a vital process providing the blood with the required amounts of oxygen. Oxygen is absorbed in the lungs in approximately 300 millions of alveoli with a total surface of 80 – 100 m². The breathing rate is regulated by blood CO_2 levels; an increase of the CO_2 concentration in the blood by 0.2 % will double it. At rest, a human being breathes 16 x per minute, consuming about 10 l/min. With increasing physical activity, the breathing rate will also increase. During heaviest work, air consumption may increase up to 100 l/min. The inhaled air has a content of 21 % oxygen and 0.04 % CO_2; the exhaled air, 17 % oxygen and 4 % CO_2. Oxygen concentrations below 15 % result in significant performance impairment with great dangers – unconsciousness, potentially with fatal consequences.

10.2 Environments for respiratory protection

The various environments for respiratory protection are shown in the overview on page 71. Within the limits of the present introduction, only filter devices (respiratory protection dependent on ambient air) and compressed air breathing apparatuses (respiratory protection independent from ambient air) will be discussed. For other fields of respiratory protection, please consult the relevant literature, e. g. the regulation «Benutzung von Atemschutzgeräten» (BGR/GUV-R 190).

10.3 Filter devices

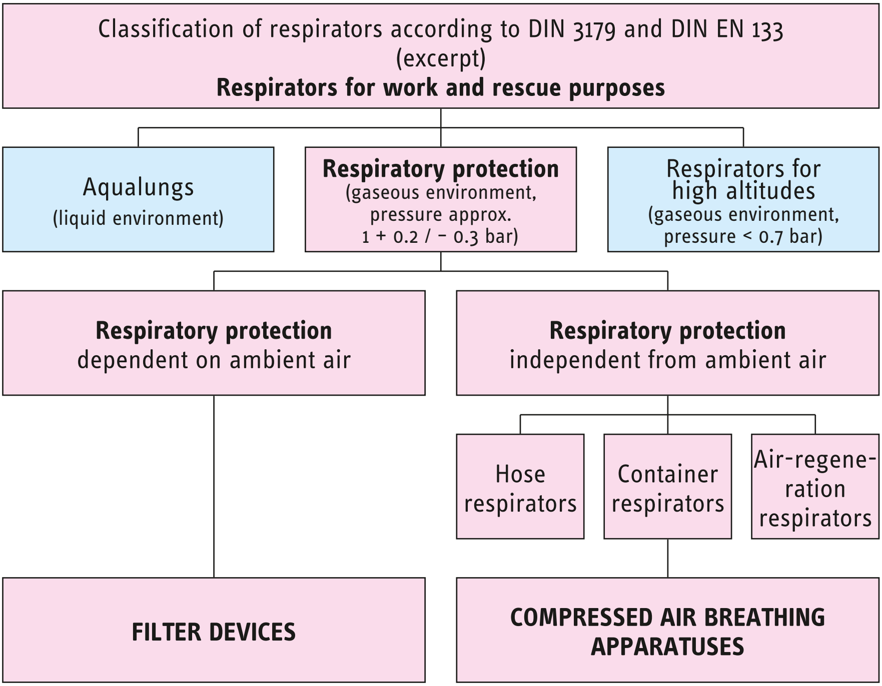
According to the regulations for the prevention of accidents and the Ordinance on Hazardous Substances, respiratory masks must be used or provided wherever during work or for rescue after a damage case the presence of noxious substances in the air must be expected.

The respirators are to be stored outside the affected areas but so that they can be reached quickly by the employees (e. g. gas mask cabinet in the corridor).

When working with pressurized gas cylinders containing any of the particularly dangerous gases hydrogen sulphide, phosphine, phosgene or hydrogen fluoride, always carry a suitable respiratory protection device (e. g. an escape filter device of ABEK filter type, see picture 21) with you to be able to escape from the danger area if needed.

Quarter masks cover mouth and nose, half masks mouth, nose and chin. However, these two mask types offer no protection against irritation or injury of the eyes.

Full masks cover the entire face, thereby offering complete protection; for this reason, they alone should be used in the laboratory (see picture 22).



Picture 21

Picture 22

In selecting the correct respiratory filter, pay attention to the following requirements:

- ▶ The oxygen concentration must be at least 17 % (v/v).
- ▶ The type and composition of noxious substances must be known, since they determine the appropriate filter type.
- ▶ The concentrations of gaseous noxious substances and particles in the air must not exceed the concentration limits listed in the following two tables.

Respiratory filters are labelled according to filter types and filter classes.

The *filter type* describes the type of noxious substance filtered from the air to be inhaled; the *filter class* describes the individual retention capacity of the respiratory filter.

An overview of commonly used filter types and filter classes is provided in the two tables below.

In *type A gas filters* (for organic substances), the filter material usually consists of activated charcoal with large specific surface to which the noxious gases are adsorbed.

In the *other gas filter types* – excluding carbon monoxide filters –, impregnated activated charcoal is used which adsorbs and chemically binds the noxious substances.

The *CO filter* contains a special catalyst (hopcalite) which converts carbon monoxide to carbon dioxide.

Filtering organic substances with a boiling point below 65 °C (low-boiling substances) poses a special problem. It has been demonstrated that such substances (such as methylene chloride or acetone) are bound only poorly by gas filters of filter type A. According to their separation behaviour (and other criteria), low-boiling substances are divided into 4 groups (see Annex B).

AX filters offer protection from low-boiling substances of classes 1 and 2.

For low-boiling substances of class 3, other filter types (*type B or K*) must be used. There are currently no suitable filters for protection from low-boiling substances of class 4.

SX filters offer protection only from individual substances listed upon the filter by the manufacturer.

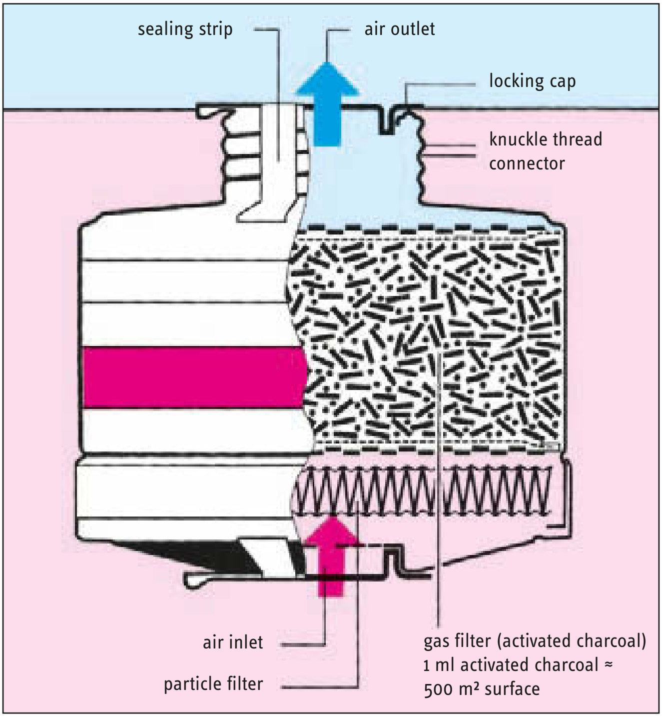
Apart from respiratory filters comprising only one filter type, there are also so-called *multi-area filters* (e. g. ABEK) available into which the individual gas filter types (in the example, A, B, E and K) are integrated.

Filter types and filter classes of gas filters according to DIN EN 141 and DIN 3181 section 3

Type	Colour coding	Main field of application	Class	Highest gas concentration permissible
A	brown	Organic gases and vapours with boiling point > 65 °C	1 2 3	1000 ml/m³ (0.1 % v/v) 5000 ml/m³ (0.5 % v/v) 10000 ml/m³ (1.0 % v/v)
B	grey	Inorganic gases and vapours, e. g. chlorine, hydrogen sulphide, hydrogen cyanide – not for carbon monoxide	1 2 3	1000 ml/m³ (0.1 % v/v) 5000 ml/m³ (0.5 % v/v) 10000 ml/m³ (1.0 % v/v)
E	yellow	Sulphur dioxide, hydrogen chloride and other acid gases	1 2 3	1000 ml/m³ (0.1 % v/v) 5000 ml/m³ (0.5 % v/v) 10000 ml/m³ (1.0 % v/v)
K	green	Ammonia and organic derivatives thereof	1 2 3	1000 ml/m³ (0.1 % v/v) 5000 ml/m³ (0.5 % v/v) 10000 ml/m³ (1.0 % v/v)
AX	brown	low-boiling organic compounds (boiling point ≤ 65 °C) of groups 1 and 2 (s. Annex B)	–	size 1 100 ml/m³ for ≤ 40 min size 1 500 ml/m³ for ≤ 20 min size 2 1000 ml/m³ for ≤ 60 min size 2 5000 ml/m³ for ≤ 20 min
SX	purple	as determined by the manufacturer	–	5000 ml/m³ (0.5 % v/v)
NO	blue	nitric oxides, e. g. NO, NO_2, NOX	–	see manufacturer’s user information
Hg	red	mercury	–	see manufacturer’s user information
CO	black	carbon monoxide	–	see manufacturer’s user information
Reactor	orange	radioactive iodine, incl. radioactive iodomethane	–	see manufacturer’s user information

Filter classes of particle filters according to DIN EN 143

Type	Colour coding	Main field of application	Class	Highest permissible concentration expressed in terms of multiples of the relevant limit value for air when using a		
				Retention capacity	half mask	full mask
P	white	Solid particles (dusts, flues) Solid particles and liquid aerosols Solid particles and liquid aerosols	1 2 3	low medium high	4 10 30	4 15 400



Picture 23:
Combination filter

Picture 24: Example for combination filter

Labelling of respiratory filters according to DIN EN 141 and DIN EN 143

Respiratory filters must be labelled.
The labelling must comprise:

- filter type
- filter class
- colour coding
- manufacturer
- reference to the applicable norm
- expiry date for storage
- note See operating instructions

Combination filters combine gas and particle filters in one casing (see picture 23). Here the air to be inhaled is first cleared from solid particles and liquid aerosols in a *particle filter*, then freed from noxious substances in the form of gases and vapours in a *gas filter.* This arrangement also offers reliable protection from volatile particles.

All prerequisites to be considered in the selection of a filter must be complied with unconditionally. For general laboratory operations, *combination filters of the multi-area type ABEK-P* are particularly well suited. However, it must be kept in mind that not even these combination filters do not protect from low-boiling substances.

The operation time of a respiratory filter depends on its absorption and retention capacity as well as on the conditions of operation. Oxygen consumption of the wearer of the respiratory mask, air temperature, air humidity, concentration and composition of the noxious substances are the limiting factors. Exhaustion of a combination filter becomes perceptible by olfactory perception and/or an increase in respiratory resistance.

The storage life of originally sealed filters is given on the filter corpus in terms of month and year. When a respiratory mask is equipped with a filter as a precaution for performing an experiment wherein hazardous substances are used, after performing the experiment without using the filter the latter is to be screwed off the mask, to be sealed with the plastic caps, and the date is to be written clearly onto the filter corpus. A filter thus labelled (exception: AX filters) can be used for another 6 months with fill performance guaranteed; then it must be replaced.

AX filters may generally be used only as delivered. Repeated usage of AX filters is permissible only within one workday (8 hours).

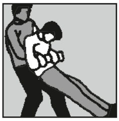
10.4 Compressed air breathing apparatuses

In case of oxygen deficiency amounting to less than 17 % (v/v) in the ambient air and/or too high concentrations of noxious substances, respiratory protection independent from ambient air must be used. Suitable devices are providing the carrier with compressed air of natural composition from a steel cylinder usually carrier on the back.

Compressed air breathing apparatuses may be used only by trained and physically able persons.

11 First Aid in case of chemical accidents

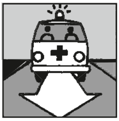
11.1 General measures



Rescue injured or poisoned persons from the danger zone, paying attention to self-protection.

The place for fist aid should be selected so that transport off to the hospital is quickly possible and no further helpers need to enter the danger zone. The First Aider must protect himself/herself if required (protective gloves, acid protection suit, respiratory protection etc.)

Emergency call
Notify emergency medical services
To be stated in the emergency call:
WHERE has it happened?
WHAT has happened?
HOW MANY people affected/injured?
WHICH kinds of injury?
WAIT for further enquiry!



Organize transport
Direct the crew of the ambulance car before the building and into it. Clear transport routes for affected/injured persons.

Request doctor
In case of any severe accident, immediately request medical assistance.

Report
All accidents must be reported to the lab head. Students in courses report to their assistant in charge.

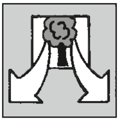
If any persons have been injured, the lab head must immediately complete an accident report and send it to the responsible insurance provider.

Particularly severe accidents, fatal accidents and mass accidents must immediately be reported to the responsible insurance provider and to the Trade Supervision Office by phone or fax. All injuries, even minor ones, must be entered into the first-aid log (BGI/GUV-I 511-1).

11.2 Immediate First Aid measures

Below some particularly important First Aid measures are listed. This list cannot replace in-depth information and in particular cannot replace practical First Aid training. Each student of chemistry is therefore requested to participate in a First Aid course. Detailed information relating to First Aid measures can be learned from the poster «Anleitung zur Ersten Hilfe bei Unfällen» (BGI/GUV-I 510-1) and the information «Erste Hilfe bei Einwirken gefährlicher chemischer Stoffe» (GUV-I 8504).

Generally, pay attention to the following:



Facilitate fresh air supply.

- Open constraining clothing.
- Remove contaminated clothing (including underwear).

- Rinse exposed skin with plenty of water.

If chemicals have got into contact with the eyes:

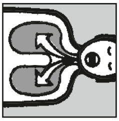
- Rinse eyes with water using an eye shower for at least 10 minutes, holding open the lid with thumb and forefinger.

- Do not allow injured persons to cool out.
- If possible, place injured persons on stretchers or blankets and cover them.

- An unconscious person must be placed in recovery position

Special cases:

In case of respiratory arrest:



In case of respiratory arrest, only immediate artificial respiration is able to save the life of the accident victim; seconds are critical.

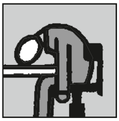
Detection:

No respiratory sounds, no respiratory movements, striking discolouration of the skin.

Measures:

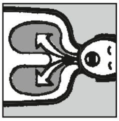
- Stretch the neck to clear the airways
- If required, remove foreign body from mouth and throat
- Kiss of life: Mouth-to-mouth or mouth-to-nose respiration

In case of unconsciousness:



Detection:

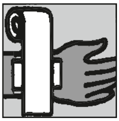
The unconscious person is not responsive.



Measures:

- Verify breathing.
- Place in recovery position.
- If breathing is not detectable, see respiratory arrest.

In case of bleeding from wounds:



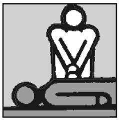
Measures:

- Cover every wound aseptically.

Almost any bleeding can be staunched using a dressing or pressure bandage.

In case of circulatory failure:

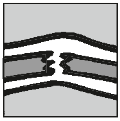
Detection:
No respiration,
no heartbeats.



Measures:

- Cardiopulmonary resuscitation

In case of bone fractures:



Measures:

- Do not move body part with fracture site.
- If injury if the spinal column is suspected, do not alter the position of the injured person.
- Fixate the position of the injured person with blankets and solid objects.
- In case of open fracture, carefully cover the wound with aseptic material.

In case of shock:

Detection:
Pulse becoming faster and weaker, finally barely palpable, pallor, cold skin, coldness, sweat on the brow, marked uneasiness.
These signs do not need to be present all together or simultaneously.

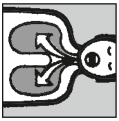
Measures:

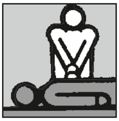
- Staunch bleeding if required.
- Shock position (lying on back, lift legs or place them in elevated position; caution: Do not use in case of fractures of legs, pelvis, spine or danger of internal injuries).
- Prevent loss of warmth.
- Provide peace and quiet.
- Pose orientation questions.
- Control pulse and respiration.

In case of accidents due to electricity:

Measures:

- Interrupt current by switching off, pulling plug, etc.
- Disconnect fuse or remove main fuse. If this is not immediately possible, pull the accident victim away from the live parts using a non-conductive object such as a dry wood bar, or by pulling his/her clothes; in doing so, take insulated position, e. g. standing upon wooden board, dry clothes or pile of newspapers.
- Do not touch anything else, in particularly not wall, rack or other persons.
- Provide peace and quiet.
- Control breathing and pulse.





- Artificial respiration in case of respiratory arrest.
- Cardiopulmonary resuscitation in case of circulatory arrest.

- In case of unconsciousness with detectable breathing: recovery position.
- Cover any burns aseptically.

In case of chemical burns:

Measures:

In case of chemical burns of the skin:

Immediately remove contaminated clothing including underwear and shoes. Rinse the skin with plenty of water.

In case of chemical burns of the eyes:

Immediately rinse the eyes with plenty of water.

In case of chemical burns of the mouth, oesophagus or stomach:

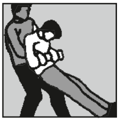
- Make the accident victim drink plenty of water in small sips.
- Do not induce vomiting under any circumstances.

In case of burns and scalds:

Measures:

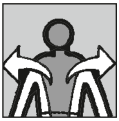
- Stop burning persons and quench the fire.
- Immediately remove clothing soaked or contaminated with hot substances.
- Immediately immerse affected body parts into cold water or hold under running cold water until pain is relieved.
- Then cover the wound aseptically (compression bandage for burns, aluminium-covered sterile gauze for burns, or the like).
- Prevent loss of warmth, cover gently.
- Do not apply ointments, powers or the like.
- Immediately transfer to medical treatment.

In case of poisoning by inhalation, skin contact or swallowing:



Measures:

- Recover the injured person from the danger zone while paying attention to self-protection.



- Immediately remove contaminated clothing, including underwear and shoes.
- Rinse skin with plenty of water.
- Control pulse and respiration.
- Provide peace and quiet.
- Protect from loss of warmth.
- When it is certain that no corrosive substance has been swallowed: induce vomiting.

After performing First Aid, immediately provide medical attention.

11.3 Frequently occurring hazard ous substances, health hazards arising from them and suitable First Aid measures

Below there are listed effects and symptoms as well as First Aid measures for several important hazardous substances. Literature:

- Information «Erste Hilfe bei Einwirkung gefährlicher chemischer Stoffe» (GUV-I 8504)
- R. Kühn, K. Birett: „Merkblätter gefährliche Arbeitsstoffe“, Ecomed Verlag, Landsberg

The First Aid measures listed in the table are intended to supplement and explain general measures, but not to replace professional medical care.

In addition, in First Aid the following general measures and notes must be observed:

- Under all circumstances, the First Aider must pay attention to protecting himself/herself.
- Rescue injured persons from the danger zone.
- Remove contaminated clothing.
- Place injured persons comfortably, and protect them from loss of warmth.
- Vomiting can be induced by stimulation of the uvula with the finger.
- If activated charcoal is administered: suspend 3 tablespoonfuls in 1 glass of water.
- If an accident victim is unconscious, do not, at any rate, induce vomiting or instil liquid. Make sure the unconscious accident victim is in recovery position.
- Oxygen may be administered only by a physician or a First Aider with additional specific training, using the designated oxygen apparatuses.

Hazardous substance	Effects/symptoms	First Aid
Acids (general)	Depending on concentration: Irritation or burn. Rash, eczema formation, skin injury. Particularly dangerous to the eyes. After swallowing, danger of gastric perforation. After resorption of larger amounts, acidosis.	➧ Rinse eyes for 10 – 15 minutes with the lids opened. ➧ Then immediately seek ophthalmologist (ambulance). ➧ Rinse skin well with plenty of water. ➧ After swallowing: make accident victim drink plenty of water, do not make any attempts at neutralisation. ➧ Do not induce vomiting!
Ammonia	Irritates the skin and mucous membranes, corrosive, toxic upon inhalation.	➧ Rinse eyes and skin with plenty of water. ➧ Remove contaminated clothing. ➧ After inhalation: Fresh air.
Arsenic	Capillary paralysis. Circulatory failure, after inhalation of dust: chest pain, after swallowing: gastric spasms, bloody diarrhoea, colic.	➧ Immediately consult physician. ➧ Gastric lavage.
Arsine	Methaemoglobin formation. Breathing difficulties, discomfort, burning sensation in the affected body parts. Several hours of latency.	➧ Rinse eyes and skin with plenty of water. ➧ After inhalation: Fresh air or oxygen.
Barium compounds	Muscular paralysis, vomiting, diarrhoea. Only soluble barium compounds are harmful; barium sulphate is not.	➧ Rinse eyes and skin with plenty of water. ➧ After swallowing: Induce vomiting, administer solution of sodium sulphate (2 – 5%).
Benzene	Slightly irritant to mucous membranes, narcotic, may cause cancer. Headache, dizziness, vomiting, state of excitation.	➧ Rinse eyes with plenty of water. ➧ Wash skin with water and soap. ➧ After inhalation: Fresh air. ➧ After swallowing: activated charcoal.
Bromine	Burns skin and mucous membranes. Burning, vesicant effects, coughing, shortness of breath, suffocation. After latency time, pulmonary oedema possible.	➧ Rinse eyes with plenty of water. (if required, wash affected skin with sodium thiosulphate solution (3%)). ➧ After inhalation: Fresh air.
Carbon monoxide	Inhibits oxygen transport in the blood. Headache, vertigo, vomiting, tinnitus, visual disturbances, excitatory states. High concentrations are lethal.	➧ Act quickly! ➧ After inhalation: fresh air or oxygen. ➧ Protect from loss of warmth.
Chlorine	Strong irritant, will burn eyes and mucous membranes. Urge to cough, suffocation. After latency time, pulmonary oedema possible.	➧ Respiratory protection for aiders! ➧ Rinse eyes with plenty of water. ➧ Wash skin with water and soap. ➧ After inhalation: Fresh air.

Hazardous substance	Effects/symptoms	First Aid
Chromates	Irritate the skin and mucous membranes, may burn and cause sores (protein precipitation by Cr(VI)). Some chromates may cause cancer.	➧ Rinse eyes with plenty of water. ➧ Wash skin with water and soap. ➧ After swallowing: Induce vomiting.
Halogenated hydrocarbons (chloroform, carbon tetrachloride, trichloroethylene, etc.)	Immediate effects: euphoria, confusion, unconsciousness (narcotic effects), respiratory paralysis, ventricular fibrillation. Damage to liver, kidney and brain possible. Cancerogenic potential suspected.	➧ Rinse eyes with plenty of water. ➧ Wash skin with water and soap. ➧ Remove contaminated clothing. ➧ After inhalation: fresh air or oxygen. ➧ After swallowing: administer activated charcoal.
Hydrochloric acid	see acids in general	
Hydrogen chloride	Strong irritant, will burn eyes and mucous membranes. Upon inhalation (possibly with latency time), difficulty to breathe. Pulmonary oedema possible.	➧ Rinse eyes and skin with plenty of water. ➧ Remove contaminated clothing. ➧ After inhalation: Fresh air.
Hydrogen cyanide (prussic acid)	Inhibition of cellular respiration, sore throat, vertigo, difficulty to breathe. Facial flushing, exhaled air reeks of bitter almond. Convulsions, unconsciousness, respiratory and circulatory failure. Fast transdermal uptake (sweating) possible.	➧ Respiratory protection for aider; act immediately! ➧ Rinse eyes and skin with plenty of water. ➧ Remove contaminated clothing. ➧ After inhalation: fresh air. If possible, oxygen via hose respirator. ➧ After swallowing: Make the accident victim drink water, induce vomiting, administer activated charcoal. ➧ In case of unconsciousness, inject 5 ml of 4-DMAP (4.dimethyl amino phenol) into the middle of the upper thigh (hydrogen cyanide kit, Blausäurebesteck) ➧ Immediate medical treatment
Hydrogen fluoride (hydrofluoric acid)	Extremely toxic and strongly corrosive. Causes deep, severe burns. Strong pain, often only after several hours. After latency time, pulmonary oedema possible.	➧ Act quickly! ➧ Rinse eyes and skin with plenty of water. ➧ Remove contaminated clothing (if required, immersion bath with calcium gluconate solution (1%)). ➧ Apply calcium gluconate gel to the affected skin. ➧ After inhalation: fresh air, absolute rest, prevent loss of warmth. ➧ After swallowing, do not induce vomiting, make accident victim drink calcium gluconate solution. ➧ Immediately transport to hospital (in recumbent position)

Hazardous substance	Effects/symptoms	First Aid
Hydrogen sulphide	Strongly irritates the mucous membranes. Neurotoxic. Urge to cough, dizziness, breathing difficulties. In higher concentrations paralysis of olfactory perception. Pulmonary oedema possible.	➧ Respiratory protection for aider! ➧ In case of eye or skin contact, rinse with plenty of water. ➧ At any rate, consult ophthalmologist (danger of cornea damage). ➧ After inhalation: fresh air, preferably oxygen. ➧ Supervision by physician.
Iodine	Irritation of skin and mucous membranes, coughing, sore throat and cold-like symptoms. Skin contact leads to depigmentation. After swallowing: strong gastrointestinal complaints, collapse.	➧ Rinse eyes with plenty of water. ➧ Wash skin with soap and water. ➧ After inhalation: fresh air. ➧ After swallowing: make accident victim drink milk.
Lye (general)	Depending on concentration: Irritation or burn. Rash, eczema formation, skin injury. Particularly dangerous to the eyes. After swallowing, danger of gastric perforation.	➧ Rinse eyes for 10 – 15 minutes with the lids opened. ➧ Then immediately seek ophthalmologist (ambulance). ➧ Rinse skin with plenty of water. ➧ After swallowing: make accident victim drink plenty of water. ➧ Do not induce vomiting!
Methanol	Unconsciousness, acidosis, blindness, vertigo, weakness, disturbances of vision, vomiting, convulsions. Keep latency in mind. May be absorbed through the skin!	➧ Rinse eyes and skin with plenty of water. ➧ After inhalation: fresh air or oxygen. Protect from loss of warmth. ➧ After swallowing: administer activated charcoal, induce vomiting, consult physician.
Nitric acid	See acids in general. Formation of nitric oxides possible (see nitric oxides).	
Nitric oxides	Irritants. Urge to cough, difficulty to breathe, after several hours of latency time pulmonary oedema possible (suffocation).	➧ Respiratory protection for aider! ➧ After inhalation: fresh air or oxygen; place comfortably. ➧ Protect from loss of warmth. ➧ Supervision by physician.
Nitrites	Danger of poisoning by methaemoglobin formation, headache, nausea, circulatory failure.	➧ After swallowing: make accident victim drink plenty of water, include vomiting.

Hazardous substance	Effects/symptoms	First Aid
Oxalic acid	Sequesters calcium from the tissues by formation of calcium oxalate. Highly corrosive, may be absorbed through the skin. After inhalation, urge to cough and breathing difficulties. After swallowing, nausea and bloody vomiting.	➧ Rinse eyes and skin with plenty of water. ➧ Remove contaminated clothing. ➧ After inhalation: fresh air or oxygen. ➧ After swallowing: make accident victim drink plenty of water and calcium gluconate solution if required.
Phosgene	Irritant. Urge to cough, lacrimation, chest pressure. After several hours of latency time, pulmonary oedema possible (danger of suffocation).	➧ Respiratory protection for aider! ➧ After inhalation: fresh air. ➧ Place comfortably. ➧ Protect from loss of warmth. ➧ Supervision by physician!
Silver nitrate	Corrosive in particular for eyes and airways. Blackening and sore formation of the skin. Burning pain in the mucous membranes, diarrhoea.	➧ Rinse eyes and skin with plenty of water. ➧ After swallowing: make accident victim drink 10% saline. ➧ Induce vomiting, rinse mouth and throat with plenty of water.
Thallium	Slow (creeping) progress of intoxication. Vomiting, idiosyncrasies of sensory nerves, alopecia.	➧ After swallowing: induce vomiting, administer activated charcoal, consult physician!
Toluene	Irritates the eyes and mucous membranes, has narcotic effects. Headache, vertigo, nausea, unconsciousness, respiratory paralysis.	➧ Rinse eyes with plenty of water. ➧ Clean skin with plenty of water and soap. ➧ After inhalation: fresh air: ➧ After swallowing: administer activated charcoal.

11.4 Immediate measures in case of accidents

1.

Rescue

- Rescue injured or poisoned persons from the danger zone, paying attention to self-protection.
- Alert the other persons in the danger zone.
- If required, switch off gas, water and electricity, using emergency cut-off if necessary.

2.

Request assistance

Enter emergency number / room number / address

First Aider: __________

Emergency medical service: __________

Fire brigade: __________

Poisoning central: __________

Ophthalmologist: __________

Surgical ambulance: __________

To be stated in the emergency call:

Where has it happened?

What has happened?

How many people affected/injured?

Which kinds of injury?

Wait for further enquiry!

3.

Provide First Aid

To be able to provide regular First Aid, you need qualification and additional training as First Aider.

Attention:

- An internal accident report must be submitted in case of any accident, even if the accident does not necessitate medical treatment (office).
- An accident report must be filed with the competent insurance provider if anybody insured has been killed or injured so badly that he/she needs medical attention.

A **form** for personal use can be found on the last page of the present brochure.

Annex A

Register of cancerogenic, mutagenic or reproduction-toxic substances (CMR register)

The following register (as of **June 2009**) lists substances which are

- classified as cancerogenic, mutagenic or reproduction-toxic in Annex I to the EC guideline 67/548/EEC (31th amendment) or
- listed in the TRGS 905 «List of cancerogenic, mutagenic or reproduction-toxic substances» (Verzeichnis krebserregender, erbgutverändernder oder fortpflanzungsgefährdender Stoffe).

The entries in the individual columns have the following meaning:

Cancerogenic

K1 Substances with known cancerogenic effects on humans. The causal connection between exposition of a person to the substance and the formation of cancer has been sufficiently demonstrated.
(R45: May cause cancer) or
(R49: May cause cancer by inhalation)

K2 Substances which should be considered as cancerogenic for humans. There are sufficient data to assume that exposition of a person to the substance may cause cancer.
(R45 or R49)
This assumption is generally based upon the following:
- suitable long term animal experiments
- other relevant information.

K3 Substances for which there is reason to suggest cancerogenic effects in humans, but for which there is insufficient information available to allow satisfactory assessment. Suitable animal models provide some suggestions which, however, are not sufficient to classify the substance as a category 2 substance.
(R40: Limited evidence of a carcinogenic effect)

Mutagenic

M1 Substances with known mutagenic effects on humans. The causal connection between exposition of a person to the substance and inheritable defects has been sufficiently demonstrated.
(R46: May cause heritable genetic damage)

M2 Substances which should be considered as mutagenic for humans. There are sufficient data to assume that exposition of a person to the substance may cause inheritable defects.
(R46: May cause heritable genetic damage). This assumption is generally based upon the following:
- suitable long term animal experiments
- other relevant information.

M3 Substances for which there is reason to suggest mutagenic effects on humans, but for which there is insufficient information available to allow satisfactory assessment. Suitable studies relating to mutagenicity provide some suggestions which, however, are not sufficient to classify the substance as a category 2 substance.
(R68: Possible risk of irreversible effects)

Reproduction-toxic

R_F Impairs fertility.

R_E Embryotoxic/foetotoxic.

R_F1 Substances with known reproduction-toxic effects on humans. The causal connection between exposition of a person to the substance and impairment of fertility has been sufficiently demonstrated.
(R60: May impair fertility)

R_E1 Substances with known embryotoxic/foetotoxic effects on humans. The causal connection between exposition of a person to the substance and harmful effects on the development of his/her immediate progeny has been sufficiently demonstrated.
(R61: May cause harm to the unborn child)

R_F2 Substances which should be considered as reproduction-toxic for humans. There are sufficient data to assume that exposition of a person to the substance may cause impair fertility. This assumption is generally based upon the following:

- demonstration, by suitable animal experiments, of an impairment of fertility without any presence of other toxic effects, or demonstration of an impairment of fertility at approximately the same dosage as causes other toxic effects, but wherein the reproduction-toxic effect observed is not a secondary consequence of the other toxic effects;

- other relevant information (R60: May impair fertility).

R_E2 Substances which should be considered as embryotoxic/foetotoxic in humans. There are sufficient data to assume that exposition of a pregnant woman to the substance may cause harmful effects on her immediate progeny. This assumption is generally based upon the following:

- demonstration, by suitable animal experiments, of embryotoxic/foetotoxic effects without any presence of significant maternal toxicity, or demonstration of embryotoxic/foetotoxic effects at a dosage causing maternal toxicity, but wherein the embryotoxic/foetotoxic effects observed are not a secondary consequence of the maternal toxicity;

- other relevant information (R61).

R_F3 Substances for which there is reason to suggest impairment of fertility in humans. This assumption is generally based upon the following:

- results from suitable animal experiments strongly suggesting impairment of fertility without any toxic effects, or providing such a suggestion at a dosage causing other toxic effects, but wherein the impairment of fertility observed is not a secondary consequence of toxicity, but wherein the findings are not sufficient for classification as R_F3;
- other relevant information (R62: Possible risk of impaired fertility).

R_E3 Substances for which there is reason to suggest embryotoxic/foetotoxic effects in humans. This assumption is generally based upon the following:

- results from suitable animal experiments strongly suggesting embryotoxic/foetotoxic effects without any presence of marked maternal toxicity, or providing such a suggestion at a dosage causing maternal toxicity, but wherein the embryotoxic/foetotoxic effects observed are not a secondary consequence of the maternal toxicity, but wherein the findings are not sufficient for classification as RE3;
- other relevant information (R63: Possible risk of harm to the unborn child).

* The classifications marked with an asterisk were taken from the TRGS 905. These national classifications by the Committee for Hazardous Substances (CHS) are made for the protection of the employees at their workplaces so the employer is enabled to implement appropriate measures. A legal classification by the EU is sought. If a legal classification by the EU already exists for any particular substance, this is to be stated upon marketing of the substance until re-evaluation of the substance by the EU commission. In this case, the classification by the CHS is to be considered when determining appropriate protective measures.

... On the basis of the available data, the substance could not be assigned to any of the categories 1 to 3 as specified in Annex VI to the guideline 67/548/EEC

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
acetaldehyde	75-07-0	3			
acetamide	60-35-5	3			
acetophenone, formaldehyde, methanol and acetic acid, reaction product of		3			
N-[2-(3-Acetyl-5-nitrothiophene-2-ylazo)-5-diethylaminophenyl]acetamide					3
acrylaldehyde	107-02-8	...	...	...	...
acrylamide	79-06-1	2	2		3
acrylnitril	107-13-1	2			
alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)-acetamide)	15972-60-8	3			
aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene) (ISO)	309-00-2	3			
5-allyl-1,3-benzodioxol	94-59-7	2	3		
4-allyl-2,6-bis(2,3-epoxypropyl)phenol; 4-allyl-6-[3-[6-[3-[6-[3-(4-allyl-2,6-bis (2,3-epoxypropyl)phenoxy)-2-hydroxypropyl]-4 allyl-2-(2,3-epoxypropyl)phenoxy]-2-hydroxypropyl]-4-allyl-2-(2,3-epoxypropyl)phenoxy]-2-hydroxypropyl]-2-(2,3-epoxypropyl) phenol; 4-allyl-6-[3-(4-allyl-2,6-bis(2,3 epoxypropyl)phenoxy) -2-hydroxypropyl]-2 (2,3-epoxypropyl)phenol; 4-allyl-6-[3-[6-[3 (4-allyl-2,6-bis(2,3-epoxypropyl)phenoxy)-2-hydroxypropyl]-4-allyl-2-(2,3-epoxypropyl)- phenoxy]-2-hydroxypropyl]-2-(2,3-epoxy propyl)phenol, mixture			3		
1-allyloxy-2,3-epoxypropane	106-92-3	2* 3	3	...	3
4-aminoazobenzene	60-09-3	2			
4-aminobiphenyl	92-67-1	1			
4-aminobiphenyl, salts of		1			
1-(2-amino-5-chlorophenyl)-2,2,2-trifluoro-1,1-ethanediol, hydrochloride; containing < 0,1 % 4-chloroaniline	214353-17-0	2			
(R,S)-2-amino-3,3-dimethylbutane amide	144177-62-8				3
6-amino-2-ethoxynaphthalene		2*			
2-(2-aminoethylamino)ethanol	111-41-1			2	3
3-amino-9-ethylcarbazole	132-32-1	2			
4-amino-3-fluorophenol	399-95-1	2			

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
5-[(4-[(7-amino-1-hydroxy-3-sulpho-2-naphthyl)azo]-2,5-[diethoxyphenyl)azo]-2-[(3 phosphonophenyl)azo]benzoic acid and 5 [(4-[(7-Amino-1-hydroxy-3-sulpho-2-naphthyl)azo]-2,5-diethoxyphenyl)azo]-3-[(3-phosphonophenyl)azo]benzoic acid, mixture	163879-69-4				3
o-aminophenol	95-55-6		3		
p-aminophenol	123-30-8		3		
amitrol (ISO)	61-82-5	...		3	
(6R−trans)-1-((7-ammonio-2-carboxylato-8-oxo-5-thia-1-azabicyclo-[4.2.0]oct-2-en-3-yl)methyl)pyridinium iodide	100988-63-4		3		
2-{4-(2-ammoniopropylamino)-6-[4-hydroxy-3-(5-methyl-2-methoxy-4-sulphamoyl phenylazo)-2-sulphonatonaphth-7-ylamino] 1,3,5-triazin-2-ylamino}-2-aminopropylhydroformiate					3
ammonium dichromate	7789-09-5	2	2	2	2
anabolics (steroid hormones)		3*	...	2*	1*
androgens (steroid hormones)		3*	...	2*	1*
androgens, weak (steroid hormones)		...	...	3*	3*
androsta-1,4,9(11)-triene-3,17-dione	15375-21-0				3
aniline	62-53-3	3	3	...	...
aniline, salts of		3	3		
antu (ISO)	86-88-4	3			
arsenous acid	36465 -76-6	1*			
arsenic acid	7778-39-4	1			
arsenic acid, salts, if not already listed		1			
drugs, cancerogenic (see TRGS 905)					
asbestos		1			
atrazine	1912-24-9	...	...		
azafenidine	68049-83-2			2	3
azobenzol	103-33-3	2	3	...	...

Name of substance	**CAS No**	**Classif./Cat.**			
		K	**M**	**R_E**	**R_F**
azo dyes azo dyes with a cancerogenic amine component (R 45). In accordance with §3 II of the Ordinance on Hazardous Substances and TRGS 905 No 4 preparations of azo dyes with a cancerogenic amine component of category 1 or 2 are to be classified as cancerogenic according to their content of cancerogenic amine which may potentially be released by reductive azo cleavage and to the content of the azo dye in the preparation (R 45).		1* or 2			
azo dyes based on benzidine, excepting those listed by name		2			
azo dyes based on 3,3'-dimethoxy benzidine		2			
azo dyes based on 3,3'-dimethyl benzidine		2			
benfuracarb (ISO)	82560-54-1				3
benomyl (ISO)	17804-35-2		2	2	2
benzidine	92-87-5	1			
benzidine, salts of		1			
benzo[a]anthracene	56-55-3	2			
benzo[b]fluoroanthrene	205-99-2	2			
benzo[j]fluoroanthrene	205-82-3	2			
benzo[k]fluoroanthrene	207-08-9	2			
benzene	71-43-2	1	2		
1,2-benzene dicarboxylic acid (phtalic acid), di-C_{6-8}-branched alkyl esters, rich in C_7 , di-iso-heptylphthalate	71888-89-6	...	...	2	3*
1,2-benzene dicarboxylic acid (phtalic acid), di-C_{7-9} branched and linear alkyl esters	68515-41-3	...	...	3*	...
1,2-benzene dicarboxylic acid (phtalic acid), di-C_{7-11}-branched and linear alkyl esters	68515-42-4	...	...	2	3
1,2-benzene dicarboxylic acid (phtalic acid), di-C_{9-11}-branched and linear alkyl esters	68515-43-5	...	...	3*	...
benzene dicarboxylic acid (phtalic acid), dipentyl ester, branched and linear n-pentyl-isopentylphthalate di-n-pentylphthalat diisopentylphthalate (DIPP)	84777-06-0 131-18-0 605-50-5	...	...	2	2
benzo[a]pyrene	50-32-8	2	2	2	2
benzo[e]pyrene	192-97-2	2			
benzoyl chloride	98-88-4	...	...	...	...
benzyl butyl phthalate	85-68-7	...	...	2	3

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
benzyl-2,4-dibromobutanoate	23085-60-1				3
benzyl violet 4B	1694-09-3	3			
succinic acid; monopersuccinic acid; dipersuccinic acid; monomethyl ester of succinic acid; monomethyl ester of persuccinic acid; dimethyl succinate; glutaric acid; monoperglutaric acid; diperglutaric acid; monomethyl ester of glutaric acid; monomethyl ester of perglutaric acid; dimethyl glutarate; adipic acid; monoperadipic acid; diperadipic acid; monomethyl ester of adipic acid; monomethyl ester of peradipic acid; dimethyl adipate; hydrogen peroxide; methanol; water; mixture of			3		
beryllium	7440-41-7	2 R49			
beryllium compounds, excepting beryllium clay silicates and those listed by name		2 R49			
beryllium oxide	1304-56-9	2 R49			
binapacryl	485-31-4			2	
biphenyl-2-ylamine	90-41-5	3			
(7-(4,6-bis-(2-ammoniopropylamino)-1,3,5-triazine-2-ylamino)-4-hydroxy-3-((2-methoxy phenyl)azo)naphthaleno-2-sulphonato)monoformiate	108225-03-2	2			
4,4'-bis(N-carbamoyl-4-methylbenzenesulphonamide)-diphenylmethane	151882-81-4	3			
bis(chloromethyl)ether	542-88-1	1			
bis(cyclopenta-1,3-dienide-bis(2,6-difluoro-3-(1H-pyrrol-1-yl)-phenolide)titan(IV)	125051-32-3				3
6,6'-bis(diazo-5,5',6,6'-tetrahydro-5,5'-dioxo)[methylene-bis(5-(6-diazo-5,6-dihydro-5-oxo-1-naphthylsulphonyloxy)-6-methyl-2-phenylene]di(naphthalene-1-sulphonate)		3			
1,3-bis(2,3-epoxypropoxy)benzene	101-90-6	2* 3	3		

Name of substance	**CAS No**	**Classif./Cat.**			
		K	**M**	**R_E**	**R_F**
bis(2-ethylhexyl)phthalate (DEHP)	117-81-7	…	…	2	2
4-[[bis-(4-fluorophenyl)methylsilyl]methyl]-4H-1,2,4-triazol; 1-[[bis-(4-fluorphenyl)-methylsilyl]methyl]-1H-1,2,4-triazol, mixture		3		2	
bis(hydroxylammonium) sulphate; hydroxylamine sulphate (2:1)	10039-54-0	3			
4,7-bis(mercaptomethyl)-3,6,9-trithia-1,11-undecanedithiol; 4,8-bis(mercaptomethyl)-3,6,9-trithia-1,11-undecanedithiol; 5,7-bis(mercaptomethyl)-3,6,9-trithia-1,11-undecanedithiol; a mixture of					3
1,2-bis(2-methoxyethoxy)ethane	112-49-2	…	…	2	3 2*
bis(2-methoxyethyl)ether	111-96-6			2	2
bis(2-methoxyethyl)phthalate	117-82-8			2	3
bis(pentabromophenyl)ether	1163-19-5	3*	…	…	…
bis(tributyltin)oxide	56-35-9			3*	2*
1,3-bis(vinylsulphonylacetamido)propane	93629-90-4		3		
lead, metal (bioavailable)	7439-92-1			1*	3*
lead copounds excepting those listed by name				1	3
lead acetate, basic	1335-32-6	3		1	3
lead alkyles $Pb(C_nH_{2n+1})_x$ (n = 1-5)				1	3
lead azide	13424-46-9			1	3
lead chromate	7758-97-6	2		1	3
lead chromate molybdate sulphate red	12656-85-8	2		1	3
lead diacetate	301-04-2			1	3
lead hexafluorosilicate	25808-74-6			1	3
lead hydrogen arsenate	7784-40-9	1		1	3
lead (II) methane sulphonate	17570-76-2			1	3
lead sulphochromate yellow	1344-37-2	2		1	3
lead tetraethyl	78-00-2			1	3
lead tetramethyl	75-74-1			1	3
lead-2,4,6-trinitroresorcinate	15245-44-0			1	3
boric acid boric acid, crude natural, containing not more than 85 per cent of H3BO3 calculated on the dry weight	10043-35-3 11113-50-1			2	2
2-bromo-2-chloro-1,1,1-trifluoroethane	151-67-7			2*	…

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
bromoethane	74-96-4	2* 3			
bromoethane	593-60-2	2			
bromoethane	74-83-9	…	3	…	…
1-bromo-2-methylpropylpropionate	158894-67-8	3			
[R]-5-bromo-3-(1-methyl-2-pyrrolidinyl-methyl)-1-H-indol	143322-57-0				3
bromoxynile (iso)	1689-84-5			3	
bromoxynile heptanoate	56634-95-8			3	
1-bromopropane	106-94-5	…	…	3	2
2-bromopropane	75-26-3				1
1-bromo-3,4,5-trifluorobenzene	138526-69-9	3			
1,3-butadiene	106-99-0	1	2		
N-butane, containing ≥ 0.1% butadiene	106-97-8	1	2		
iso-butane, containing ≥ 0.1% butadiene	75-28-5	1	2		
2-butanonoxime	96-29-7	3			
1,4-butansultone	1633-83-6	3*			
2,4-butansultone	1121-03-5	2*			
2-butenal	4170-30-3 123-73-9	…	3	…	…
1-butoxy-2,3-epoxypropan	2426-08-6	3	2* 3	…	…
1-tert-butoxy-2,3-epoxypropane	7665-72-7	…	3*	…	…
4’-tert-butyl-2’-6’-dimethyl-3’-5’-dinitro-acetophenone, Musk Ketone	81-14-1	3	…	…	…
2-(4-tert-butylphenyl)ethanol	5406-86-0				3
5-tert-butyl-2,4,6-trinitro-m-xylene, Musk Xylene	81-15-2	3	…	…	…
2-butyryl-3-hydroxy-5-thiocyclohexan-3-yl-cyclohex-2-en-1-one	94723-86-1				2
5-(3-butyryl-2,4,6-trimethylphenyl)-2-[1-(ethoxyimino)propyl]-3-hydroxycyclohex-2-N-1-on	138-164-12-2			3	3
cadmium	7440-43-9	2	3	3	3
cadmium chloride	10108-64-2	2	2	2	2
cadmium cyanide	542-83-6	2*			
cadmium fluoride	7790-79-6	2	2	2	2
cadmium formiate	4464-23-7	2*			
cadmium hexafluorosilicate	17010-21-8	2*			

Name of substance	**CAS No**	**Classif./Cat.**			
		K	**M**	**R_E**	**R_F**
cadmium iodide	7790-80-9	2*			
cadmium oxide	1306-19-0	2	3	3	3
cadmium sulphate	10124-36-4	2	2	2	2
cadmium sulphide	1306-23-6	2	3	3	3
cadmium compounds, with the exception of those listed by name (bioavailable in the form of inhalable dusts/aerosols)		2*			
calcium chromate	13765-19-0	2			
calcium salicylates (branched C_{10-14} and C_{18-30} alkylated); calcium phenates (branched C_{10-14} and C_{18-30} alkylated); calcium sulphurised phenates (branched C_{10-14} and C_{18-30} alkylated), a mixture of:					3
camphechlor (toxaphene)	8001-35-2	3			
captafol (ISO)	2425-06-1	2			
captan	133-06-2	3			
carbadox (INN)	6804-07-5	2			
carbaryl (1-naphthyl methylcarbamate)	63-25-2	3			
carbendazime (ISO)	10605-21-7		2	2	2
4,4'-carbonimidoylbis (N,N-dimethylaniline)	492-80-8	2* 3	3*	...	...
4,4'-carbonimidoylbis(N,N-dimethylaniline), synthesis (see also TRGS 906)					
4,4'-carbonimidoylbis(N,N-dimethylaniline), salts (excepting hydrochloride)		3			
4,4'-carbonimidoylbis-(N,N-dimethylaniline) hydrochloride	2465-27-2	2* 3	3*	...	...
2-chloroacetaldehyde	107-20-0	3	...	...	...
2-chloroacetamide	79-07-2	...	...	...	3
chloroalkanes, C_{10-13} Cl_{1-13}	85535-84-8	3			
cis-1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride	51229-78-8			3	
4-chloroaniline	106-47-8	2			
4-chlorobenzotrichloride	5216-25-1	2	...	...	3 2*
2-chloro-1,3-butadiene	126-99-8	2	...	...	...
chlordane (ISO)	57-74-9	3			
chlordecone (ISO)	143-50-0	3			
5-chloro-1,3-dihydro-2H-indol-2-one)	1763-75-0				3

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
chlordimeform (ISO)	6164-98-3	3			
chlordimeform hydrochloride	19750-95-9	3			
chloro-N,N-dimethylformiminium chloride	3724-43-4			2	
1-chloro-2,3-epoxypropane	106-89-8 51594-55-9	2			
chloroethane	75-00-3	3			
chloro-1-ethylcyclohexylcarbonate	99464-83-2		3		
(2-chloroethyl)(3-hydroxypropyl)ammonium chloride	40722-80-3	2	2		
6-(2-chloroethyl)-6-(2-methoxyethoxy)-2,5,7,10-tetraoxa-6-silaundecane	37894-46-5			2	
3-chloro-4-(3-fluorobenzyloxy)aniline	202197-26-0		3		
chlorofluoromethane	593-70-4	2*			
2-chloro-6-fluorophenol	2040-90-6		2		3
(3-chloro-2-hydroxypropyl)trimethyl-ammonium chloride	3327-22-8	3	...	...	...
chloromethane	74-87-3	3			
chloromethyl methyl ether	107-30-2	1			
3-chloro-2-methylpropene	563-47-3	3*			
1-chloro-2-nitrobenzene	88-73-3	3*	...	...	3*
1-chloro-4-nitrobenzene	100-00-5	3	3	...	...
1-(4-chlorophenyl)-4,4-dimethyl-3 (1,2,4-triazole-1-ylmethyl)-pentane-3-ol	1075 34-96-3			3	
3-(4-chlorophenyl)-1,1-dimethyluronium-trichloracetate	140-41-0	3			
(2RS,3SR)-3-(2-chlorophenyl)-2-(4-fluorophenyl)-[(1H-1,2,4-triazol-1-yl)methyl]oxirane	133855-98-8	3		3	3
4-[(3-chlorophenyl)(1*H*-imidazol-1-yl)methyl]-1,2-benzenediamine dihydrochloride	159939-85-2				3
(3-chlorophenyl)-(4-methoxy-3-nitrophenyl)methanone	66938-41-8		3		
3-chloropropene	107-05-1	3	3		
chlorpropham (ISO); isopropyl 3-chlorocarbanilate	101-21-3	3			
chlorothalonile	1897-45-6	3			
4-chloro-o-toluidine	95-69-2	1* 2	3		
4-chloro-o-toluidine, hydrochloride	3165 -93-3	1* 2	3		
5-chloro-o-toluidin	95-79-4	3*			

Name of substance	**CAS No**	**Classif./Cat.**			
		K	**M**	**R_E**	**R_F**
α-chlorotoluenes, mixtures		1*			
α-chlorotoluene	100-44-7	2	3*	3*	...
chlorotolurone	15545-48-9	3		3	
chlozolinate	84332-86-5	3			
chrome(III)chromate	24613-89-6	2			
chromoxychloride	14977-61-8	2 R49	2		
chrome trioxide	1333-82-0	1	2		3
chrome(VI) compounds, excepting barium chromate and those listed by name		2 R49			
chrysene	218-01-9	2	3		
chrysoidine; 4-(phenylazo)benzene-1,3-diamine	495-54-5	...	3		
chrysoidine monohydrochloride; 4-phenylazophenylene-1,3-diamine monohydrochloride	532-82-1		3		
chrysoidine monoacetate; 4-(phenylazo)benzene-1,3-diamine monoacetate	75660-25-2				
chrysoidine acetate; 4-(phenylazo)benzene-1,3-diamine acetate	79234-33-6				
chrysoidine-p-dodecylbenzenesulphonate; dodecylbenzenesulphonic acid, compound with 4-(phenylazo) benzene-1,3-diamine (1:1)	63681-54-9				
chrysoidine dihydrochloride; 4-(phenylazo)benzene-1,3-diamine dihydrochloride	83968-67-6				
chrysoidine sulphate; bis[4-(phenylazo)benzene-1,3-diamine] sulphate	84196-22-5				
chrysoidine C10-14-alkyl derivatives; benzenesulphonic acid, mono-C10-14-alkyl derivatives, compounds with 4-(phenylazo)-1,3-benzenediamine; chrysoidine compound with dibutylnaphthalene sulphonic acid; dibutylnaphthalenesulphonic acid, compound with 4-(phenylazo)benzene-1,3-diamine (1:1)	85407-90-5 94247-67-3		3		
C.I. Basic Red 9	569-61-9	2	...	...	...
C.I. Basic Violet 3 (methyl violet)	548-62-9	3	...	...	...
C.I. Basic Violet 3 with ≥ 0,1 % of Michler's Ketone	548-62-9	2			

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
C.I. Direct Blue 218	73070-37-8	3*	…	…	…
cinidon ethyl (ISO)	142891-20-1	3			
cobalt, metal (bioavailable, in the form of inhalable dusts/aerosols) with the exception of hard alloys	7440-48-4	3*	…	…	…
cobalt acetate	71-48-7 6147-53-1	2 R49	3	…	2
cobalt carbonate	513-79-1	2 R49	3	…	2
cobalt dichloride	7646-79-9	2 R49	3	…	2
cobalt lithium nickel oxide		1 R49			
ccbalt-nickel-gray-periklas; C.I. Pigment black 25; C.I. 77332; cobalt-nickel-dioxide; cobalt-nickel-oxide	68186-89-0 58591-45-0 12737-30-3	1 R49			
cobalt(II)nitrate	10141-05-6 10026-22-9	2 R49	3	…	2
cobalt oxide (bioavailable, in the form of inhalable dusts/aerosols)	1307-96-6	3*	…	…	…
cobalt sulphate	10124-43-3	2 R49	3	…	2
cobalt(II)sulphate heptahydrate	10026-24-1	2 R49	3	…	2
cobalt sulphide (bioavailable, in the form of inhalable dusts/aerosols)	1317-42-6	3*	…	…	…
cobalt compounds (bioavailable, in the form of inhalable dusts/aerosols), excepting those listed by name		3*	…	…	…
colchicine	64-86-8		2		
cristobalite (see TRGS 906)	14464-46-1				
4-cyan-2,6-diiodophenyloctanoate	3861-47-0			3	
cyclohexanone	108-94-1	…			
cycloheximide	66-81-9		3	2	
cyclohexylamine	108-91-8				3
N-cyclohexyl-N-methoxy-2,5-dimethyl-3-furamide	60568-05-0	3			
trans-4-cyclohexyl-L-proline monohydro-chloride	90657-55-9				3
1-cyclopropyl-6,7-difluoro-1,4-dihydro-4-oxoquinoline-3-carboxylic acid	93107-30-3				3

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
cyproconazole	94361-06-5			3	
daminozide	1596-84-5	…			
DDT	50-29-3	3			
N,N’-diacetylbenzidine	613-35-4	2	3		
diallat (ISO)	2303-16-4	3			
2,4-diaminoanisol sulphate	615-05-4 39156-41-7	2	3		
3,3’-diaminobenzidine	91-95-2	2	3		
3,3’-diaminobenzidine, salts		3*			
4,4’-diaminodiphenylmethane	101-77-9	2	3		
diammonium 1-hydroxy-2-(4-(4-carboxyphenylazo)-2,5-dimethoxyphenylazo)-7-amino-3-naphthalenesulphonate					3
diammonium nickel hexacyanoferrate	74195-78-1	1 R49			
diantimon trioxide	1309-64-4	3			
diarsenic pentoxide	1303-28-2	1			
diarsenic trioxide	1327-53-3	1			
diazomethane	334-88-3	2			
dibenz[a,h]anthracene	53-70-3	2			
dibor trioxide	1303-86-2			2	2
1,2-dibromo-3-chloropropane	96-12-8	2	2	…	1
2,6-dibromo-4-cyanphenyloctanoate	1689-99-2			3	
1,2-dibromomethane	106-93-4	2			
2,2-dibromo-2-nitroethanol	69094-18-4	3			
2,3-dibromopropan-1-ol	96-13-9	2	…	…	3
dibutylphthalate (DBP)	84-74-2	…	…	2	2* 3
dibutyltin dichloride	683-18-1		3	2	2
dibutyltin hydrogen borate	75113-37-0		3	2	2
dichloraocetylene	7572-29-4	2* 3			
3,3’-dichlorobenzidine	91-94-1	2			
3,3’-dichlorobenzidine, salts		2			
1,4-dichlorobenzene	106-46-7	3	…		

Name of substance	**CAS No**	**Classif./Cat.**			
		K	**M**	**R_E**	**R_F**
2,2’-[(3,3’-dichloro[1,1’-biphenyl]-4,4’-diyl)bis(azo)]bis[N-(2,4-dimethylphenyl)]-3-oxo-butanamide; 2-[[3,3’-dichloro-4’-[[1[[(2,4-dimethylphenyl)amino]carbonyl]-2-oxopropyl]azo]-[1,1’-biphenyl]-4-yl]azo]-N-(2-methylphenyl)-3-oxo-butanamide; 2-[[3,3’-dichloro-4’-[[1[[(2,4-dimethylphenyl)amino]-carbonyl]-2-oxopropyl]azo][1,1’-biphenyl]-4-yl]azo]-N-(2-carboxylphenyl)-3-oxo-butanamide, mixture of		3			
1,4-dichlorobut-2-en	764-41-0	2			
2,2’-dichlorodiethyl ether	111-44-4	3			
2,2’-dichlorodiethyl sulphide	505-60-2	1*			
3,5-dichloro-N-(1,1-dimethylprop-2-inyl)benzamide	23950-58-5	3			
1,2-dichloroethane	107-06-2	2			
1,1-dichloroethene	75-35-4	3			
dichloromethane	75-09-2	3			
1,2-dichloromethoxy ethane	41683-62-9	...	3*	...	...
2,2’-dichloro-4,4’-methylene dianiline	101-14-4	2			
2,2’-dichloro-4,4’-methylene dianiline, salts		2			
3-(3,5-dichlorophenyl)-2,4-dioxo-N-isopro-pylimidazolidine-1-carboxamide	36734-19-7	3			
(+/-) 2-(2,4-dichlorophenyl)-3-(1H-1,2,4-triazol-1-yl)propyl-1,1,2,2-tetrafluoroethylether	112281-77-3	...			
1,2-dichloropropane	78-87-5	...	...	...	...
1,3-dichlore-2-propanol	96-23-1	2			
1,3-dichlorepropene (cis- and trans-)	542-75-6	2*	3*	...	...
2,3-dichloropropene	78-88-6		3		
α, α-dichlorotoluene	98-87-3	3			
2,2-dichloro-1,1,1-trifluorethane	306-83-2	3*	...	...	...
dicyclohexylnitrosamine	947-92-2	...	3*	...	...
dieldrin (ISO)	60-57-1	3			
1,2,3,4-diepoxybutane	1464-53-5	2	2	...	3*
diesel engine emissions		2*			
diester of 4,4'-methylenebis[2-(2-hydroxy-5-methylbenzyl)-3,6-dimethylphenol] and 6-diazo-5,6-dihydro-5-oxonaphthalene-1-sulphonic acid (1:2); triester of 4,4'-methylenebis[2-(2-hydroxy-5-methylbenzyl)-3,6-dimethylphenol] and 6-diazo-5,6-dihydro-5-oxonaphthalene-1-sulphonic acid (1:3); a mixture of		3			

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
1,2-diethoxyethane	629-14-1			2	3
diethylcarbamidic acid chloride	88-10-8	3			
diethyl sulphate	64-67-5	2	2		
1,1-difluoroethene	75-38-7	3*			
diglycidyl ether	2238-07-5	3*			
N,N’-dihexadecyl-N,N’-bis(2-hydroxyethyl)-propane diamide	149591-38-8				3
N-[6,9-dihydro-9-[[2-hydroxy-1-(hydroxymethyl)ethoxy]methyl]-6-oxo-1H-purin-2-yl]acetamide	84245-12-5	2	2	2	2
(S)-2,3-dihydro-1H-indol-2-carboxylic acid	79815-20-6				3
1,4-dihydroxybenzene	123-31-9	3	3	...	...
4-[4-(1,3-dihydroxyprop-2-yl)-phenylamino]-1,8-dihydroxy-5-nitroanthraquinone	114565-66-1	3			
diisobutyl phthalate	84-69-5			2	3
toluene-2,4-di-isocyanate	584-84-9	3			
toluene-2,6-di-isocyanate	91-08-7	3			
reaction products of diisopropanolamine with formaldehyde (1:4)	220444-73-5	3			
3,3'-dimethoxybenzidine	119-90-4	2			
3,3'-dimethoxybenzidine, salts of		2			
1,2-dimethoxyethane	110-71-4	...	...	2	2
N,N-dimethylacetamide	127-19-5			2	3*
(E)-3-[1-[4-[2-(dimethylamino)ethoxy]phenyl]-2-phenylbut-1-enyl]phenol	82413-20-5	3			2
N,N-(dimethylamino)thioacetamide hydrochloride	27366-72-9			2	
N,N-dimethylaniline	121-69-7	3	...	...	...
N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate	118612-00-3	3			
3,3'-dimethylbenzidine	119-93-7	2			
3,3'-dimethylbenzidine, salts of		2			
dimethylcarbamoyl chloride	79-44-7	2			
N,N-dimethyl formamide	68-12-2			2	
1,2-dimethyl hydrazine	540-73-8	2			
N,N-dimethyl hydrazine	57-14-7	2			
dimethyl hydrogen phosphite	868-85-9	3*			

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
dimethyl(2-(hydroxymethylcarbamoyl)ethyl)phosphonate; diethyl (2-(hydroxymethylcarbamoyl)ethyl)phosphonate; methyl ethyl (2-(hydroxymethylcarbamoyl) ethyl)phosphonate; a mixture of		2	2		
dimethyl sulphamoyl chloride	13360-57-1	2			
dimethyl sulphate	77-78-1	2	3		
dimoxystrobin (ISO); (E)-2-(methoxyimino)-N-methyl-2-[α-(2,5-xylyloxy)-o-tolyl]acetamide	149961-52-4	3		3	
disodium-4-amino-3-[[4'-[(2,4-diaminophenyl)azo] [1,1'-biphenyl]-4-yl]azo] 5-hydroxy-6-(phenyl)azo)naphthalene 2,7-disulphonate	1937-37-7	2		3	
disodium-3,3'-[[1,1'-biphenyl]-4,4'-diylbis-(azo)]bis(4-amino-naphthalen-1-sulphonate)	573-58-0	2		3	
disodium-[5-[(4'-((2,6-dihydroxy-3-((2-hydroxy-5-sulphophenyl)azo)phenyl)azo)-(1,1'-biphenyl)-4-yl)azo]salicylato (4-)] cuprate(2-)	16071-86-6	2			
disodium 4-(3-ethoxycarbonyl-4-(5-(3-ethoxycarbonyl-5-hydroxy-1-(4-sulphonatophenyl)pyrazol-4-yl)penta-2,4-dienylidene)-4,5-dihydro-5-oxopyrazol-1-yl)benzenesulphonate; trisodium 4-(3-ethoxycarbonyl-4-(5-(3-ethoxycarbonyl-5-oxido-1-(4-sulphonatophenyl)pyrazol-4-yl)penta-2,4-dienylidene)-4,5-dihydro-5-oxopyrazol-1-yl)benzenesulphonate; reaction mass of				2	
disodium tetraborate, anhydrous; -decahydrate -pentahydrate	1330-43-4 1303-96-4 12179-04-3			2	2
dinickel hexacyanoferrate	14874-78-3	1 R49			
dinickel trioxide	1314-06-3	1 R49			
dinitronaphthalene, all isomers	27478-34-8	3*			
2,3-dinitrotoluene	602-01-7	2	3		3
2,4-dinitrotoluene	121-14-2	2	3		3
2,5-dinitrotoluene	619-15-8	2	3		3
2,6-dinitrotoluene	606-20-2	2	3		3
3,4-dinitrotoluene	610-39-9	2	3		3
3,5-dinitrotoluene	618-85-9	2	3		3
dinitrotoluenes (techn. isomer mixtures)	25321-14-6	2	3	...	3
dinocarb	39300-45-3			2	
dinoseb	88-85-7			2	3

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
dinoseb, salts and esters, excepting those listed by name				2	3
dinoterb	1420-07-1			2	
dinoterb, salts and esters				2	
1,4-dioxane	123-91-1	3			
1,3-diphenylguanidine	102-06-7				3
diuron	330-54-1	3			
divanadium pentaoxide	1314-62-1		3	3	
DNOC	534-52-1		3		
dodecachlorpentacyclo[5.2.1.0^{2,6}.0^{3,9}.0^{5,8}]decane	2385-85-5	3		3	3
edifenphos	17109-49-8		...		
1,2-epoxybutane	106-88-7	2* 3			
1-epoxyethyl-3,4-epoxycyclohexane	106 87 6	2* 3			
1,2-epoxy-3-phenoxypropane	122-60-1	2	3		
2,3-epoxy-1-propanol R-2,3-epoxy-1-propanol	556-52-5 57044-25-4	2	3	...	2
1,2-epoxy-3-(tolyloxy)propane	26447-14-3 2186-24-5 2186-25-6 2210-79-9	3*	3		
erionite	12510-42-8	1			
estrogens (steroid hormones)		3*	...	3*	1*
estrogens, weak (steroid hormones)		...	...	3*	3*
cyclic 3-(1,2-ethanediylacetale)-estra-5(10),9(11)-diene-3-17-dione	5571-36-8				2
ethylene	74-85-1	...	3*	...	...
O,O'-(ethenylmethylsilylen)di[(4-methylpentan-2-on)oxime]					3
ethidium bromide; 3,8-diamino-1-ethyl-6-phenylphenantridiniumbromide	1239-45-8		3		
4-ethoxyaniline	156-43-4		3		
4'-ethoxy-2-benzimidazol-anilide	120187-29-3		3		
2-ethoxyethanol	110-80-5			2	2
2-ethoxyethyl acetate	111-15 -9			2	2
(4-ethoxyphenyl)(3-(4-fluoro-3-phenoxyphenyl)propyl)dimethylsilane	105024-66-6				2

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole	2593-15-9	3			
ethyl 1-(2,4-dichlorophenyl)-5-(trichloromethyl)-1H-1,2,4-triazole-3-carboxylate	103112-35-2	2			
ethyleneimine	151-56-4	2	2		
ethylen oxide	75-21-8	2	2		
ethylene thiourea	96-45-7	3*	...	2	
2-ethylhexane-1,3-diol	94-96-2			...	
2-ethylhexanoic acid	149-57-5			3	
2-ethylhexyl-[[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-methyl]thio]acetate	80387-97-9			2	
2-ethylhexyl-2-ethylhexanoate	7425-14-1			3	
3-ethyl-2-methyl-2-(3-methylbutyl)-1,3-oxa-zolidine	143860-04-2				2
1-ethyl-1-methylmorpholinium bromide	65756-41-4		3		
4-ethyl-4-methylpyrrolidinium bromide	69227-51-6		3		
2-ethylphenylhydrazine hydrochloride	19398-06-2	3			
fibre dusts, inorganic (classification depends on fulfilment of certain criteria, see TRGS 905 section 2.3) asbestos, erionite, mineral wool and ceramic mineral fibres: see there		2* or 3*			
fenarimol	60168-88-9			3	3
fenpropimorph	67564-91-4			3	
fenthion	55-38-9		3		
fentin acetate	900-95-8	3		3	
fentin hydroxide	76-87-9	3		3	
fluazifop-butyl	69806-50-4			2	
fluazifop-P-butyl	79241-46-6			3	
flumioxazine	103361-09-7			2	
1-(4-fluoro-5-hydroxymethyl-tetrahydrofuran 2-yl)-1H-pyrimidine-2,4-dione	41107-56-6		3		
flusilazol	85509-19-9	3		2	
forchlorfenuron (ISO)	68157-60-8	3			
formaldehyde	50-00-0	3			
formamide	75 -12-7			2	
furaldehyde	98-01-1	3	...	...	...
furane	110-00-9	2	3	...	...

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
furfuryl alcohol	98-00-0	3			
gestagens (steroid hormones)		3*	...	2*	1*
gestagens, weak (steroid hormones)		...	...	3*	3*
glucocorticoides (steroid hormones)		...	...	1*	3*
glufosinat-ammonium (ISO)	77182-82-2			3	2
6-glycidyloxynapht-1-yl-oxymethyloxirane	27610-48-6		3		
glycidyltrimethylammonium chloride	3033-77-0	2	3	...	3
glyoxal	107-22-2		3		
heptachlor (ISO)	76-44-8	3			
heptachlor epoxide	1024-57-3	3			
hexachlorobenzene	118-74-1	2			
1,1,2,3,4,4-hexachloro-1,3-butadiene	87-68-3	3*			
1,2,3,4,5,6-hexachlorocyclohexanes, excepting those listed by name		3			
hexahydrocyclopenta[c]pyrrol-1-(1H)-ammonium-N-ethoxycarbonyl-N-(p-tolylsulphonyl)azanide			3		
hexamethylphosphoric acid triamide	680-31-9	2	2		
n-hexane	110-54-3				3
2-hexanone	591-78-6				3
O-hexyl-N-ethoxycarbonylthiocarbamate		2	2		
wood dusts (excepting hard wood dusts, see there)		3*			
hydrazine	302-01-2	2			
hydrazine, salts		2			
hydrazine bis(3-carboxy-4 hydroxybenzolsulphonate)		2			
(4-hydrazinophenyl)-N-methylmethansulphonamide hydrochloride	81880-96-8		3		
hydrazine trinitromethane		2			
hydrazobenzene	122-66-7	2			
2-[2-hydroxy-3-(2-chlorophenyl)carbamoyl-1-naphthylazo]-7-[2-hydroxy-3-(3-methylphenyl)carbamoyl-1-naphthylazo]fluoren-9-one				2	
2-(2-hydroxy-3,5-dinitroanilino)ethanol	99610-72-7				3
6-hydroxy-1-(3-isopropoxypropyl)-4 methyl-2-oxo-5-[4-(phenylazo)phenylazo] 1,2-dihydro-3-pyridincarbonitrile	85136-74-9	2			
hydroxylamine	7803-49-8	3			

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
hydroxylammonium chloride	5470-11-1	3			
hydroxylammonium hydrogensulphate	10046-00-1	3			
hydroxylamine phosphate	20845-01-6	3			
hydroxylamine dihydrogenphosphate	19098-16-9	3			
hydroxylamine-4-methylbenzenesulphonate	53933-48-5	3			
hydroxylammonium nitrate	13465-08-2	3			
N-[3-hydroxy-2-(2-methyl-acryloylaminomethoxy)-propoxymethyl]-2-methyl acrylamide; N-[2,3-bis(2-methyl-acryl-oylamino-methoxy)propoxymethyl]-2 methyl-acrylamide; methacrylamid; 2-methyl-N-(2-methyl-acryloylamino methoxy-methyl)-acrylamide; N-(2,3 dihydroxy-propoxymethyl)-2-methyl-acrylamide, mixtures		2	3		
N-[4-[(2-hydroxy-5-methylphenyl)azo]phenyl]acetamide, C.I. Disperse yellow 3	2832-40-8	3			
4-(7-hydroxy-2,4,4-trimethyl-2-chromanyl) resorcinol-4-yl-tris(6-diazo-5,6-dihydro-5 oxonaphthalene-1-sulphonate) and 4-(7-hydroxy 2,4,4-trimethyl-2-chromanyl)resorcinol-bis(6-diazo-5,6-dihydro-5-oxonaphthalene-1 sulphonate), mixture 2:1	140698-96-0	3			
ioxynil	1689-83-4			3	
O-isobutyl-N-ethoxy carbonylthiocarbamate	103122-66-3	2	2		
4,4'-isobutylethylidenediphenol	6807-17-6				2
isobutylnitrite	542-56-3	2	3		
2-(isocyanatosulphonylmethyl) benzoic acid methyl ester	83056-32-0		3		
isoprene, methyl-1,3-butadiene	78-79-5	2	3	…	…
4,4'-isopropylidendiphenol	80-05-7			…	3
isoproturone	34123-59-6	3			
isoxaflutole	141112-29-0			3	
potassium bromate	7758-01-2	2			
potassium chromate	7789-00-6	2 R49	2		
potassium dichromate	7778-50-9	2	2	2	2
potassium 1-methyl-3-morpholinocarbonyl-4-[3-(1-methyl-3-morpholinocarbonyl-5-oxo-2-pyrazolin-4-ylidene)-1-propenyl] pyrazole-5-olate; containing ≥ 0,5 % N,N-dimethylformamide	183196-57-8			2	
potassium nitrate	775 7-79-1			…	…
potassium titanium oxide (K2Ti6O13)	12056-51-8	3			

Name of substance	**CAS No**	**Classif./Cat.**			
		K	**M**	**R_E**	**R_F**
Ceramic mineral fibres Fibres for special applications [Artificially produced, undirected glassy (silicate) fibres comprising no more than 18 % (w/w) of alkali metal and alkaline earth metal oxides ($Na_2O+K_2O+CaO+MgO+BaO$)] (classification depends on fulfilment of certain criteria)		2 R49			
ketoconazole; 1-[4-[4-[[(2SR,4RS)-2-(2,4-dichlorophenyl)-2-(imidazol-1-ylmethyl)-1,3-dioxolan-4-yl]methoxy]phenyl]piperazin-1-yl]ethanone	65277-42-1				2
silicic acid, lead nickel salt	68130-19-8	1 R49		1	3
carbon disulphide	75-15-0			3	3
carbon monoxide	630-08-0			1	
kresoxim-methyl	143390-89-0	3			
slimes and sludges, copper electrolytic refining, decopperised, nickel sulphate	92129-57-2	1 R49	3	2	
slimes and sludges, copper electrolyte refining, decopperised	94551-87-8	1 R49	3	1	3
lindane	58-89-9	3*	...		
linurone (ISO)	330-55-2	3		2	3
malachite green hydrochloride, C.I. Basic Green 4	569-64-2 18015-76-4			3	
mancozeb	8018-01-7			3	
maneb	12427-38-2			3	
mepanipyrim	110235-47-7	3			
4-mesyl-2-nitrotoluene	1671-49-4				3
metconazole (ISO); (1RS,5RS;1RS,5SR)-5-(4-chlorobenzyl)-2,2-dimethyl-1-(1H-1,2,4-triazol-1-ylmethyl)cyclopentanol	125116-23-6			3	
2-methoxyaniline	90-04-0	2	3		
methoxyacetic acid	625-45-6			2	2
2-methoxyethanol	109-86-4			2	2
2-(2-methoxyethoxy)ethanol	111-77-3			3	
2-methoxyethyl acetate	110-49-6			2	2
(Z)-2-methoxymino-2-[2-(tritylamino)-thiazol-4-yl]acetic acid	64485-90-1	3			
7-methoxy-6-(3-morpholin-4-yl-propoxy)-3H-quinazolin-4-one; containing < 0,5 % formamide	199327-61-2			2	

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
2-methoxy-1-propanol	1589-47-5	…		2	…
2-methoxypropyl acetate-1	70657-70-4			2	
6-methoxy-m-toluidine 2-methoxy-5-methylaniline	120-71-8	2			
N-methylacetamide	79-16-3	…	…	2	…
methylacrylamidomethoxy acetate (containing ≥ 0.1% acrylamide)	77402-03-0	2	2		
methylacrylamidoglycolate; containing ≥ 0.1% acrylamide	77402-05-2	2	2		
methylacrylate	96-33-3	…			
2-methylaziridine	75-55-8	2			
(methyl-ON N-azoxy)methylacetate	592-62-1	2		2	
N-methylbis(2-chloroethyl)amine	51-75-2	1*	2*		
2-methyl-5-tert-butylthiophenol				3	
6-methyl-1,3-dithiolo(4,5-b)-quinoxaline-2-one	2439-01-2				3
4,4’-methylenebis(2-ethylaniline)	19900-65-3	3	…	…	…
reaction product of 4,4’ methylenebis[2-(4-hydroxybenzyl)-3,6-dimethylphenol] and 6-diazo-5,6-dihydro 5-oxo-naphthalenesulphonate (1:2); reaction product of 4,4’-methylenbis[2-(4-hydroxybenzyl)-3,6-dimethylphenol] and 6-diazo-5,6-dihydro-5-oxo-naphthalenesulphonate (1:3); mixture of		3			
(methylenebis(4,1-phenyleneazo(1-(3-(dimethylamino)propyl)-1,2-dihydro-6 hydroxy-4-methyl-2-oxopyridine-5,3-diyl))) 1,1’-dipyridiniumdichloride dihydrochloride		2			
4,4'-methylenediphenyl diisocyanate; diphenylmethane-4,4’-diisocyanate; 2,2’-methylenediphenyl diisocyanate; diphenylmethane-2,2’-diisocyanate; o-(p-isocyanatobenzyl)phenyl isocyanate; diphenylmethane-2,4’-diisocyanate; methylenediphenyl diisocyanate	101-68-8 2536-05-2 5873-54-1 26447-40-5	3	…	…	…
4,4’-methylenediphenyldiisocyanate tech. (polymeric) MDI, pMDI (in the form of inhalable aerosols, fraction A)	9016-87-9	3*	…	…	…
4,4’-methylene-di-o-toluidine	838-88-0	2			
N-methylformamide	123-39-7			2	
methyl iodide	74-88-4	3			

Name of substance	**CAS No**	**Classif./Cat.**			
		K	**M**	**R_E**	**R_F**
methyl isocyanate	624-83-9			3	
1-methyl-3-nitro-1-nitrosoguanidine	70-25-7	2			
N-methylolchloroacetamide	2832-19-1	...	3*		...
diaminotoluene; (technical product - mixture of 4-methyl-m-phenylene diamine and 2-methyl-m-phenylene diamine)		2	3		3
2-methyl-m-phenylendiamine	823-40-5		3		
4-methyl-m-phenylendiamine	95-80-7	2	3		3
4-methyl-m-phenylendiamine sulphate	65321-67-7	2			
N-methyl-2-pyrrolidone	872-50-4			2	
N-methyl-2,4,6-N-tetranitroaniline	479-45-8	...	...	...	...
Michler's Ketone	90-94-8	2	3	...	...
mineral wool Artificially produced, undirected glassy (silicate) fibres comprising more than 18 % (w/w) of alkali metal and alkaline earth metal oxides (Na2O+K2O+CaO+MgO+ BaO); classification depends on fulfilment of certain criteria		2* 3			
molinat	2212-67-1	3			3
molybdenum trioxide	1313-27-5	3			
monocrotophos	6923-22-4		3		
monuron (ISO)	150-68-5	3			
morpholin-4-carbonyl chloride	15159-40-7	2* 3			
myclobutanil	88671-89-0			3	
naphthalene	91-20-3	3	...	...	...
2-naphthylamine	91-59-8	1			
2-naphthylamine, salts		1			
1,5-naphthylendiamine	2243-62-1	3			
1-(1-naphthylmethyl)quinolinium chloride	65322-65-8	3	3		
sodium bisulphite	7631-90-5		...		
sodium chromate	7775-11-3	2	2	2	2
sodium dichromate	105 88-01-9	2	2	2	2
sodium dichromate dihydrate	7789-12-0	2	2	2	2
sodium metabisulphite	7681-57-4			...	
sodium nitrate	7631-99-4		...	...	

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
sodium perborate;	15120-21-5			2	3
perboric acid, sodium salt;	11138-47-9				
perboric acid,sodium salt, monohydrate;	12040-72-1				
sodium peroxometaborate;	7632-04-4				
perboric acid (HBO(O_2)),	10332-33-9				
sodium salt, monohydrate;					
sodium peroxoborate;					
[containing < 0,1 % (w/w) of particles with an aerodynamic diameter of below 50 μm					
nickel, metal	7440-02-0	3			
nickel salts, soluble, unless listed separately		1*	…		
dialuminium nickel tetraoxide;	12004-35-2	1			
nickel titanium trioxide;	12035-39-1	R49			
nickel titanium oxide;	12653-76-8				
nickel divanadium hexaoxide;	52502-12-2				
cobalt dimolybdenum nickel octaoxide;	68016-03-5				
nickel zirkonium trioxide;	70692-93-2				
molybdenum nickel tetraoxide;	14177-55-0				
nickel tungsten tetraoxide;	14177-51-6				
olivine, nickel green;	68515-84-4				
lithium nickel dioxide;	12031-65-1				
molybdenum nickel oxide	12673-58-4				
nickel barium titanium	68610-24-2	1			
primrose priderite;		R49			
C.I. Pigment Yellow 157;					
C.I. 77900					
nickel bis(4-cyclohexylbutyrate)	3906-55-6	1	3	2	
		R49			
nickel bis(sulphamidate);	13770-89-3	1	3	2	
nickel sulphamate		R49			
nickel bis(tetrafluoroborate)	14708-14-6	1	3	2	
		R49			
nickel boride (NiB);	12007-00-0	1			
dinickel boride;	12007-01-1	R49			
trinickel boride;	12007-02-2				
nickel boride;	12619-90-8				
dinickel silicide;	12059-14-2				
nickel disilicide;	12201-89-7				
dinickel phosphide;	12035-64-2				
nickel boron phosphide	65229-23-4				
nickel carbonate;	3333-67-3	1	3	2	
basic nickel carbonate	16337-84-1	R49			

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
nickel chromate	14721-18-7	1 R49			
nickel di(acetate); nickel acetate	373-02-4 14998-37-9	1 R49	3	2	
nickel diarsenide; nickel arsenide	12068-61-0 27016-75-7	1 R49			
nickel dibenzoate	553-71-9	1 R49	3	2	
nickel dichlorate; nickel dibromate; ethyl hydrogen sulphate, nickel(II)salt	67952-43-6 14550-87-9 71720-48-4	1 R49	3	2	
nickel dichloride	7718-54-9	1 R49	3	2	
nickel dichromate	15586-38-6	1 R49	3	2	
nickel dicyanide	557-19-7	1 R49			
nickel difluoride nickel dibromide nickel diiodide nickel potassium fluoride	10028-18-9 13462-88-9 13462-90-3 11132-10-8	1 R49	3	2	
nickel diformate; formic acid, nickel salt; formic acid, copper nickel salt	3349-06-2 15843-02-4 68134-59-8	1 R49	3	2	
nickel dihydroxide	12054-48-7 11113-74-9	1 R49	3	2	
nickel dipotassium bis(sulphate); diammonium nickel bis(sulphate)	13842-46-1 15699-18-0	1 R49	3	2	
nickel dilactate	16039-61-5	1 R49	3	2	
nickel dinitrate; nitric acid, nickel salt	13138-45-9 14216-75-2	1 R49	3	2	
nickel dioxide	12035-36-8	1 R49			
nickel diperchlorate; perchloric acid, nickel(II) salt	13637-71-3	1 R49	3	2	
nickel dithiocyanate	13689-92-4	1 R49	3	2	
nickel hexafluorosilicate	26043-11-8	1 R49	3	2	

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F

nickel hydrogen phosphate;
nickel bis(dihydrogen phosphate);
trinickel bis(orthophosphate);
dinickel diphosphate;
nickel bis(phosphinate);
nickel phosphinate;
phosphoric acid, calcium nickel salt;
diphosphoric acid, nickel(II) salt
	14332-34-4
	18718-11-1
	10381-36-9
	14448-18-1
	14507-36-9
	36026-88-7
	17169-61-8
	19372-20-4
		1
		R49			

nickel matte, calcination or electrolytic raffination		1			
nickel monoxide; nickel oxide; bunsenite	1313-99-1 11099-02-8 34492-97-2	1 R49			
nickel(II) octanoate	4995-91-9	1 R49	3	2	
nickel oxalate; oxalic acid, nickel salt	547-67-1 20543-06-0	1 R49			
nickel selenate	15060-62-5	1 R49	3	2	
nickel selenide	1314-05-2	1 R49			
nickel(II) selenite	10101-96-9	1 R49			
nickel(II) silicate; dinickel orthosilicate; nickel silicate (3:4); silicic acid, nickel salt; trihydrogen hydroxybis[orthosilicato-4-)]trinickelate(3-)	21784-78-1 13775-54-7 31748-25-1 37321-15-6 12519-85-6	1 R49			
nickel(II) stearate; nickel(II) octadecanoate	2223-95-2	1 R49	3	2	
nickel sulphate	7786-81-4	1 R49	3	2	
nickel (II) sulphide; nickel sulphide; millerite	16812-54-7 [1] 11113-75-0 [2] 1314-04-1	1 R49	3		
nickel(II) sulphite; nickel tellurium trioxide; nickel tellurium tetraoxide; molybdenum nickel hydroxide oxide phosphate	7757-95-1 15851-52-2 15852-21-8 68130-36-9	1 R49			
nickel telluride	12142-88-0	1 R49			
nickel tetracarbonyl	13463-39-3	3		2	

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F

nickel(II) trifluoroacetate;
nickel(II) propionate;
nickel bis(benzenesulphonate);
nickel(II) hydrogen citrate;
citric acid, ammonium nickel salt;
citric acid, nickel salt;
nickel bis(2-ethylhexanoate);
2-ethylhexanoic acid, nickel salt;
dimethylhexanoic acid nickel salt;
nickel(II) isooctanoate;
nickel isooctanoate;
nickel bis(isononanoate);
nickel(II) neononanoate;
nickel(II) isodecanoate;
nickel(II) neodecanoate;
neodecanoic acid, nickel salt;
nickel(II) neoundecanoate;
bis(D-gluconato-O1,O2)nickel;
nickel 3,5-bis(tert-butyl)-4-hydroxybenzoate (1:2);
nickel(II) palmitate;
(2-ethylhexanoato-O)(isononanoato-O)nickel;
(isononanoato-O)(isooctanoato-O)nickel;
(isooctanoato-O)(neodecanoatoO)nickel;
(2-ethylhexanoato-O)(isodecanoatoO)nickel;
(2-ethylhexanoato-O)(neodecanoatoO)nickel;
(isodecanoato-O)(isooctanoatoO)nickel;
(isodecanoato-O)(isononanoatoO)nickel;
(isononanoato-O)(neodecanoatoO)nickel;
fatty acids, C6-19-branched, nickel salts;
fatty acids, C8-18 and C18-unsaturated,
nickel salts;
2,7-naphthalenedisulphonic acid, nickel(II) salt;
	16083-14-0
	3349-08-4
	39819-65-3
	18721-51-2
	18283-82-4
	22605-92-1
	4454-16-4
	7580-31-6
	93983-68-7
	29317-63-3
	27637-46-3
	84852-37-9
	93920-10-6
	85508-43-6
	85508-44-7
	51818-56-5
	93920-09-3
	71957-07-8
	52625-25-9
	13654-40-5
	85508-45-8
	85508-46-9
	84852-35-7
	84852-39-1
	85135-77-9
	85166-19-4
	84852-36-8
	85551-28-6
	91697-41-5
	84776-45-4
	72319-19-8
		1
		R49
			3	2	

nickel triuranium decaoxide	15780-33-3	1 R49			
nickel tin trioxide; nickel stannate	12035-38-0	1 R49			
5-nitroacenaphthene	602-87-9	2			
2-nitro-4-aminophenol	119-34-6	3*			
2-nitroanisole	91-23-6	2			
nitrobenzene	98-95-3	3			3
4-nitrobiphenyl	92-93-3	2			
nitrofen (2,4-Dichlorphenyl-4'-nitrophenyl ether) (ISO)	1836-75-5	2		2	

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
1-nitronaphthalene	86-57-7	…	…	…	…
2-nitronaphthalene	581-89-5	2			
2-nitro-p-phenylendiamine	5307-14-2	3*			
2-nitropropane	79-46-9	2			
nitropyrenes (mono, di, tri, tetra) isomers	5522-43-0	3*			
N-nitrosodi-n-butylamine	924-16-3	2*			
N-nitrosodiethanolamine	1116-54-7	2			
N-nitrosodiethylamine	55-18-1	2*			
N-nitrosodimethylamine	62-75-9	2			
N-nitroso-di-i-propylamine	601-77-4	2*			
N-nitrosodi-n-propylamine	621-64-7	2			
N-nitroso-ethylphenylamine	612-64-6	2*			
N-nitroso-methylethylamine	10595-95-6	2*			
N-nitrosomethylphenylamine	614-006	2*			
N-nitrosomethylphenylamine	59-89-2	2*			
p-nitrosophenol	104-91-6		3		
N-nitrosopiperidine	100-75-4	2*			
N-nitrosopyrrolidine	930-55-2	2*			
5-nitro-o-toluidine, 2-amino-4-nitrotoluene	99-55-8	3	…	…	…
5-nitro-o-toluidine hydrochloride	51085-52-0	3	…	….	…
2-nitrotoluene	88-72-2	2	2	…	3
nonylphenol/linear side chain	25154-52-3	…	…	3	3
4-nonylphenol, branched side chain	84852-15-3	…	…	3	3
octabromodiphenylether	32536-52-0	…	…	2	3
octamethylcyclotetrasiloxane, D4	556-67-2	…	…	…	3
olaquindox	23696-28-8	3*	2*	…	3*
orthoboric acid, sodium salt	13840-56-7			2	2
oxadiargyle (3-[2,4-dichloro-5-(2-propynyloxy)phenyl]-5-(1,1-dimethylethyl)-1,3,4-oxadiazol-2(3H)-one)	39807-15-3			3	
oxirane methanol, 4-methylbenzenesulphonate, (S)-	70987-78-9	2	3		
3-oxoandrost-4-ene-17-β-carbolic acid	302-97-6				3
4,4'-oxydianiline and salts thereof	101-80-4	2	2	…	3
ozone	10028-15-6	3*	…	…	…

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
passive smoking (measures for the protection of employees at the workplace are regulated by the Labour Protection Act and the Health and Safety at Work Ordinance)		1*	3*	1	...
pentachloroethane	76-01-7	3			
pentachlorophenol	87-86-5	2* 3	3*	2*	...
pentachlorophenol, salts of		2*			
pentachlorophenol, alkali salts of - sodium salt - potassium salt	131-52-2 7778-73-6	2* 3			

perboric acid (H3BO2(O2)), monosodium salt trihydrate;
perboric acid, sodium salt, tetrahydrate;
perboric acid (HBO(O2)), sodium salt, tetrahydrate; sodium peroxoborate hexahydrate;
	13517-20-9
	37244-98-7
	10486-00-7
				2	3

perfluorooctane sulphonic acid; heptadecafluorooctane-1-sulphonic acid; potassium perfluorooctanesulphonate; potassium heptadecafluorooctane-1-sulphonate; diethanolamine perfluorooctane sulphonate; ammonium perfluorooctane sulphonate; ammonium heptadecafluorooctanesulphonate; lithium perfluorooctane sulphonate; lithium heptadecafluorooctanesulphonate	1763-23-1 2795-39-3 70225-14-8 29081-56-9 29457-72-5	3		2	
peracetic acid	79-21-0	...	...	...	...
phenol	108-95-2	......	3	...	......
phenolphthalein	77-09-8	2	3		3
4-phenylazophenylene-1,3-diaminomonohydrochloride	532-82-1	...	3*		
1-phenylazo-2-naphthol	842-07-9	3	3	...	...
(4-phenylbutyl)phosphinic acid	86552-32-1	3			
4,4'-(1,3-phenylene-bis(1-methylethylidene))bisphenol	13595-25-0				3
1,2-phenylene diamine	95-54-5	3	3	...	...
1,2-phenylene diamine dihydrochloride	615-28-1	3	3	...	...
1,3-phenylene diamine	108-45-2	...	3	...	...
1,3-phenylene diamine dihydrochloride	541-69-5	...	3	...	...
1,4-phenylene diamine	106-50-3	...	...	...	...
1,4-phenylene diamine dihydrochloride	624-18-0	...	...	...	...

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
(R)-α-phenylethylammonium-(-)-(1R, 2S)-(1,2-epoxypropyl)-phosphonate monohydrate	25383-07-7				3
phenylhydrazine	100-63-0	2	3	...	...
phenylhydrazine hydrochloride	27140-08-5	2	3		
phenylhydrazinium chloride	59-88-1	2	3	...	...
phenylhydrazinium sulphate, 2:1	52033-74-6	2	3		
N-phenyl-2-naphthylamine	135-88-6	3			
trans-4-phenyl-L-proline	96314-26-0				3
phosphamidones	13171-21-6		3		
phoxim (ISO)	14816-18-3				3
piperazine; [solid]	110-85-0			3	3
piperazine hydrochloride; piperazine dihydrochloride; piperazine phosphate	6094-40-2 142-64-3 1951-97-9			3	3
3-(piperazin-1-yl)-benzo[d]isothiazole hydrochloride	87691-88-1				3
polychlorated biphenyls	1336-36-3	3*		2*	2*
profoxydim (ISO)	139001-49-3	3		3	
3-propanolide	57-57-8	2			
1,3-propanesulphone	1120-71-4	2			
propargite (2-(4-tert-butylphenoxy)cyclohexyl-prop-2-ynyl sulphite)	2312-35-8	3			
propazine (2,4-bis(isopropylamino)-6-chloro-1,3,5-triazine)	139-40-2	3			
1,2-propylene oxide	75-56-9	2	2		
propylene thiourea	2122-19-2			3	
isopropyl glycidyl ether	4016-14-2	...	3*	...	...
pymetrozine	123312-89-0	3			
pyrogallic acid (1,2,3-trihydroxybenzene)	87-66-1		3		
pyrolysis products of organic substances, see also those listed by		1* or 2*			
quartz A dust (see also TRGS 906)	14808-60-7				
mercury	7439-97-6			2	
mercury dichloride	7487-94-7		3		3
quinoline	91-22-5	2	3		
simazine (6-chloro-N,N’-diethyl-1,3,5-triazine-2,4-diamine)	122-34-9	3			

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
strontium chromate	7789-06-2	2			
styrene oxide	96-09-3	2			
sulphallate (2-chloroallyl-N,N-diethyldithiocarbamate) (ISO)	95-06-7	2			
1,4,5,8-tetraaminoanthraquinone	2475-45-8	2	…	…	…
tepraloxydim (ISO)	149979-41-9	3		3	3
tetraboron disodium heptaoxide, hydrate	12267-73-1			2	2
5,6,12,13-tetrachloroanthra(2,1,9-def:6,5,10-d'e'f')diisoquinoline-1,3,8,10(2H,9H)-tetrone	115662-06-1				3
2,3,7,8-tetrachlorodibenzo-p-dioxine	1746-01-6	2*			
1,1,2,2-tetrachloroethane	79-34-5	3*	3*	…	…
tetrachloroethene	127-18-4	3	…	3*	…
tetrachloromethane	56-23-5	3			
N,N,N’,N’-tetraglycidyl-4,4’-diamino 3,3’-diethyldiphenyl-methane	130728-76-6		3		
tetrahydro-1,3-dimethyl-1Hpyrimidin-2-one; dimethyl propyleneurea	7226-23-5				3
(±) -tetrahydrofurfuryl-(R)-2-[4-(6-chloro-quinoxaline-2-yloxy)-phenyloxy]propanoate	119738-06-6		3	2	3
tetrahydrothiopyrane-3-carboxaldehyde	61571-06-0			2	
tetrakis(hydroxymethyl)phosphonium chloride; reaction product with urea and distilled hydrated C16-18-tallow alkylamine	166242-53-1	3	…		
N,N,N’,N’-tetramethylacridine-3,6-yldiamine hydrochloride and N,N,N’,N-tetramethylacridine-3,6-diaminomonohydrochloride compound with ZnCl2 (acridine orange)	65-61-2 10127-02-3	…	3*	…	…
2,2’-((3,5’,5,5’-tetramethyl-(1,1’-biphenyl)- 4,4’-diyl)-bis(oxymethylene))-bisoxiran	85954-11-6	3			
N,N,N’,N’-tetramethyl-4,4’-methylene-dianiline, 4,4’-methylenbis(N,N-dimethylaniline)	101-61-1	2			
tetrasodium-3,3’-[[1,1’-biphenyl]-4,4’-diylbis(azo)]bis[5-amino 4-hydroxy-naphthalene-2,7-disulphonate]	2602-46-2	2		3	
tetranitromethane	509-14-8	2*			
thioacetamide	62-55-5	2			
4,4’-thiodianiline and its salts	139-65 -1	2			
thiourea	62-56-6	3		3	

Name of substance	CAS No	Classif./Cat.			
		K	M	R_E	R_F
thiophanate-methyl (dimethyl 4,4'-o-phenylenebis[3-thioallophanate])	23564-05-8		3		
thirame (bis(dimethylthiocarbamoyl)disulphide)	137-26-8		...		
o-toluidine	95-53-4	2			
p-toluidine	106-49-0	3	...	...	...
p-toluidinium chloride	540-23-8	3			
p-toluidine sulphate	540-25-0	3			
toluene	108-88-3	...	...	3	...
4-o-tolylazo-o-toluidine	97-56-3	2			
m-tolylidene diisocyanate	26471-62-5	3			
triammonium 6-amino-3-((2,5-diethoxy-4-(3-phosphonophenyl)azo)phenyl) azo-4-hydroxy-2-naphthalenesulphonate; diammonium 3-((4-((7-amino-1-hydroxy-3-sulpho-naphthalen-2-yl)azo)-2,5-diethoxyphenyl)azo)benzoate, mixture of					3
triammonium 4-[4-[7-(4-carboxylatoanilino)-1-hydroxy-3-sulphonato-2-naphthylazo]-2,5-dimethoxyphenylazo]benzoate	221354-37-6				3
1,2,4-triazole	288-88-0			3	
trilead-bis(orthophosphate)	7446-27-7			1	3
tribromomethane	75-25-2	3*			
tributyl phosphate	126-73-8	3			
2,3,4-trichloro-1-butene	2431-50-7	2* 3			
1,1,2-trichlorethane	79-00-5	3	...	...	...
trichloroethylene	79-01-6	2	3		
trichloromethane	67-66-3	2* 3	3*	3*	...
N-(trichloromethylthio)phthalimide	133-07-3	3			
2,4,6-trichlorophenol	88-06-2	3			
1,2,3-trichloropropan	96-18-4	2	3*	...	2
α, α, α-trichlorotoluene	98-07-7	2			
tridemorph (2,6-dimethyl-4-tridecylmorpholine)	24602-86-6			2	
triethyl arsenate	15606-95-8	1			
trifluoroiodomethane	2314-97-8		3		
trifluralin (ISO) (containing < 0.5 ppm NPDA)	1582-09-8	3			

Name of substance	**CAS No**	**Classif./Cat.**			
		K	**M**	**R_E**	**R_F**
2,4,5-trimethylaniline hydrochloride	137-17-7 21436-97-5	2	...	...	...
3,5,5-trimethyl-2-cyclohexen-1-one	78-59-1	3	...	...	...
trimethylphosphate	512-56-1	3*	2*		
trimethylopropane tri(3-aziridinylpropanoate) (TAZ)	52234-82-9		3		
trisodium-[4’-(8-acetylamino-3,6-disulphonato-2-naphthylazo)-4’’-(6-benzoyl amino-3-sulphonato-2-naphthylazo)-biphenyl-1,3’,3’’,1’’’-tetraolato-O,O’,O’’,O’’’] copper (II)	164058-22-4	2			
trisodium-bis[7-acetamido-2 (4-nitro-2-oxidophenylazo)-3-sulphonato 1-naphtholato]chromate(1-)			3		
trisodium nitrilotriacetate	5064-31-3	3			
trinickel bis(arsenate); nickel(II) arsenate	13477-70-8	1			
trinickel bis(arsenite)	74646-29-0	1 R49			
trinickel disulphide	12035-72-2 12035-71-1	1 R49	3		
trinickel tetrasulphide	12137-12-1	1 R49			
2,4,7-trinitrofluoren-9-on	129-79-3	3*			
2,4,6-trinitrotoluene (and isomers in technical mixtures)	118-96-7	3*			
1,3,5-trioxane	110-88-3	...	...	3	...
1,3,5-tris(3-aminomethylethylphenyl)-1,3,5 (1H,3H,5H)-triazine-2,4,6-trione and oligomer mixtures of 3,5-bis(3-aminomethylphenyl)-1-poly[3,5-bis(3-aminomethylphenyl)-2,4,6-triazine-1,3,5-(1H,3H,5H)triazine 1-yl]-1,3,5-(1H,3H,5 H)-triazin-2,4,6-trione, mixture		2		2	
tris(2-chloroethyl)phosphate	115-96-8	2* 3	...	3	2
1,3,5-tris-[(2S and 2R) -2,3-epoxypropyl]1,3,5-triazin-2,4,6-(1H, 3H, 5H)-trione	59653-74-6		2		
N,N’,N’-tris(2-methyl-2,3-epoxypropyl)-perhydro-2,4,6-oxo-1,3,5-triazine	26157-73-3		3		
1,3,5-tris(oxiranylmethyl)-1,3,5-triazine-2,4,6(1H,3H,5H)trione	2451-62-9	...	2	...	3*
ethyl carbamate (INN)	51-79-6	2			
valinamide	20108-78-5				3
vinclozoline (3-(3,5-dichlorophenyl)-5-methyl- 5-vinyloxazolidine-2,4-dione)	50471-44-8	3		2	2
vinyl acetate	108-05-4	3*			

Name of substance	**CAS No**	**Classif./Cat.**			
		K	**M**	**R_E**	**R_F**
9-vinyl carbazole	1484-13-5	...	3	...	...
vinyl chloride	75-01-4	1			
4-vinylcyclohexen	100-40-3	3*	...	...	3*
N-vinyl-2-pyrrolidone	88-12-0	3	...	...	...
warfarin	81-81-2 5543-57-7 5543-58-8			1	
hydrogen peroxide	7722-84-1	...	...	...	...
2,4-xylidine	95-68-1	3*			
2,6-xylidine	87-62-7	3	...	...	...
zinc chromates, including zinc potassium chromate		1			
zirame (zinc dimethyldithiocarbamate)	137-30-4			...	

Source: IFA – Institute for Occupational Safety and Health of the German Social Accident Insurance, St. Augustin/Germany

Annex B

Classification of organic compounds with a boiling point ≤ 65 °C (low-boiling substances) into filter groups

Groups 1 and 2:
Low-boiling substances against which protection can be effected by an AX filter.

Group 3:
Low-boiling substances against which protection can be effected using other gas filters (such as type B or K).

Group 4:
Low-boiling substances which cannot be bound sufficiently by gas filters.

Low-boiling substances of groups 1 to 4

Group 1

acetaldehyde
2-amino-butane
2-amino-2-methyl-propane
2-bromo-2-chloro-1,1,1,-trifluoroethane
bromomethane
1,3-butadiene
1-chloro-1,1-difluoroethane
chlorofluoromethane
2-chloro-1,3-butadiene
3-chloro-1-propene
1,1,-dichloro-ethene
dichloromethane
diethyl amine
1,1,-difluoroethene
dimethyl ether
1,1,-dimethylethylamino(tert-butylamine)
1,2-epoxy-propane
ethane thiole
ethylene oxide
iodomethane
methanol
monochloro dimethyl ether
2-propenal (acrolein)
propylene imine
trichloromethane
vinyl chloride

Group 2

acetone
bromomethane
butane
chloroethane
2-chloropropane
1,3-cyclopentadiene
dibromodifluoromethane
1,1-dichloroethane
1,1-dichloroethene (cis)
1,1-dichloroethene (trans)
1,2-dichlor-1,1,2,2,-tetrafluoroethane
diethyl ether
dimethoxy methane
dimethyl propane
1,3-epoxy-propane
ethyl formiate
glyoxal
methyl acetate
methyl butane
methyl formiate
methyl propane
n-pentane
propanal

Group 3

2-amino-propane
carbon disulphide
carbonyl chloride (phosgene)
cyanogen
diazo methane
dimethyl amine
1,1-dimethyl hydrazine
ethyl amine
ethyl dimethyl amine
    (N,N-dimethyl ethyl amine)
ethylene imine
ethyl mercury chloride
formaldehyde
methanethiol
methyl amine
methyl isocyanate

Group 4

bromotrifluoromethane
chlorodifluoromethane
chloromethane
chlorotrifluoromethane
dichlorodifluoromethane
dichlorofluoromethane
1,1-difluoroethene
ketene
methyl acetylene
propane
trichlorofluoromethane
1,1,2-trichloro-1,2,2-trifluoroethane

Annex C

Danger symbols and danger indicators

E

explosive

F+

extremely flammable

F

highly flammable

O

flammable

T+

very toxic

T

toxic

Xn

harmful

Xi

irritant

C

corrosive

N

harmful to the
environment

Indicators of special dangers (R phrases)

R1	Explosive when dry
R2	Risk of explosion by shock, friction, fire or other sources of ignition
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition
R4	Forms very sensitive explosive metallic compounds
R5	Heating may cause an explosion
R6	Explosive with or without contact with air
R7	May cause fire
R8	Contact with combustible material may cause fire
R9	Explosive when mixed with combustible material
R10	Flammable
R11	Highly flammable
R12	Extremely flammable
R14	Reacts violently with water
R15	Contact with water liberates extremely flammable gases
R16	Explosive when mixed with oxidising substances
R17	Spontaneously flammable in air
R18	In use, may form flammable/explosive vapour-air mixture
R19	May form explosive peroxides
R20	Harmful by inhalation
R21	Harmful in contact with skin
R22	Harmful if swallowed
R23	Toxic by inhalation
R24	Toxic in contact with skin
R25	Toxic if swallowed
R26	Very toxic by inhalation
R27	Very toxic in contact with skin
R28	Very toxic if swallowed
R29	Contact with water liberates toxic gas.
R30	Can become highly flammable in use
R31	Contact with acids liberates toxic gas
R32	Contact with acids liberates very toxic gas
R33	Danger of cumulative effects
R34	Causes burns
R35	Causes severe burns
R36	Irritating to eyes
R37	Irritating to respiratory system
R38	Irritating to skin
R39	Danger of very serious irreversible effects
R40	Limited evidence of a carcinogenic effect
R41	Risk of serious damage to eyes
R42	May cause sensitisation by inhalation

R43	May cause sensitisation by skin contact
R44	Risk of explosion if heated under confinement
R45	May cause cancer
R46	May cause heritable genetic damage
R48	Danger of serious damage to health by prolonged exposure
R49	May cause cancer by inhalation
R50	Very toxic to aquatic organisms
R51	Toxic to aquatic organisms
R52	Harmful to aquatic organisms
R53	May cause long-term adverse effects in the aquatic environment
R54	Toxic to flora
R55	Toxic to fauna
R56	Toxic to soil organisms
R57	Toxic to bees
R58	May cause long-term adverse effects in the environment
R59	Dangerous for the ozone layer
R60	May impair fertility
R61	May cause harm to the unborn child
R62	Possible risk of impaired fertility
R63	Possible risk of harm to the unborn child
R64	May cause harm to breast-fed babies
R65	Harmful: may cause lung damage if swallowed
R66	Repeated exposure may cause skin dryness or cracking
R67	Vapours may cause drowsiness and dizziness
R68	Possible risk of irreversible effects

Combinations of R phrases

R14/15	Reacts violently with water, liberating extremely flammable gases
R15/29	Contact with water liberates toxic, extremely flammable gases
R20/21	Harmful by inhalation and in contact with skin
R20/22	Harmful by inhalation and if swallowed
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed
R21/22	Harmful in contact with skin and if swallowed
R23/24	Toxic by inhalation and in contact with skin
R23/25	Toxic by inhalation and if swallowed
R23/24/25	Toxic by inhalation, in contact with skin and if swallowed
R24/25	Toxic in contact with skin and if swallowed
R26/27	Very toxic by inhalation and in contact with skin
R26/28	Very toxic by inhalation and if swallowed
R26/27/28	Very toxic by inhalation, in contact with skin and if swallowed

R27/28	Very toxic in contact with skin and if swallowed
R36/37	Irritating to eyes and respiratory system
R36/38	Irritating to eyes and skin
R36/37/38	Irritating to eyes, respiratory system and skin
R37/38	Irritating to respiratory system and skin
R39/23	Toxic: danger of very serious irreversible effects through inhalation
R39/24	Toxic: danger of very serious irreversible effects in contact with skin
R39/25	Toxic: danger of very serious irreversible effects if swallowed
R39/23/24	Toxic: danger of very serious irreversible effects through inhalation and in contact with skin
R39/23/25	Toxic: danger of very serious irreversible effects through inhalation and if swallowed
R39/24/25	Toxic: danger of very serious irreversible effects in contact with skin and if swallowed
R39/23/24/25	Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed
R39/26	Very Toxic: danger of very serious irreversible effects through inhalation
R39/27	Very Toxic: danger of very serious irreversible effects in contact with skin
R39/28	Very Toxic: danger of very serious irreversible effects if swallowed
R39/26/27	Very Toxic: danger of very serious irreversible effects through inhalation and in contact with skin
R39/26/28	Very Toxic: danger of very serious irreversible effects through inhalation and if swallowed
R39/27/28	Very Toxic: danger of very serious irreversible effects in contact with skin and if swallowed
R39/26/27/28	Very Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed
R42/43	May cause sensitization by inhalation and skin contact
R48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation
R48/21	Harmful:danger of serious damage to health by prolonged exposure in contact with skin
R48/22	Harmful:danger of serious damage to health by prolonged exposure if swallowed
R48/20/21	Harmful:danger of serious damage to health by prolonged exposure through inhalation and in contact with skin

R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R48/21/22	Harmful:danger of serious damage to health by prolonged exposure in contact with skin and if swallowed
R48/20/21/22	Harmful:danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation
R48/24	Toxic: danger of serious damage to health by prolonged exposure in contact with skin
R48/25	Toxic: danger of serious damage to health by prolonged exposure if swallowed
R48/23/24	Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin
R48/23/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R48/24/25	Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed
R48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R68/20	Harmful: possible risk of irreversible effects through inhalation
R68/21	Harmful: possible risk of irreversible effects in contact with skin
R68/22	Harmful: possible risk of irreversible effects if swallowed
R68/20/21	Harmful: possible risk of irreversible effects through inhalation and in contact with skin
R68/20/22	Harmful: possible risk of irreversible effects through inhalation and if swallowed
R68/21/22	Harmful: possible risk of irreversible effects in contact with skin and if swallowed

R68/20/21/22

Harmful possible risk of irreversible effects through inhalation, in contact with skin and if swallowed

Safety advice (S phrases)

(S1)	Keep locked up
(S2)	Keep out of the reach of children
S3	Keep in a cool place
S4	Keep away from living quarters
S5	Keep contents under ... (appropriate liquid to be specified by the manufacturer)
S6	Keep under ... (inert gas to be specified by the manufacturer)
S7	Keep container tightly closed
S8	Keep container dry
S9	Keep container in a well-ventilated place
S12	Do not keep the container sealed
S13	Keep away from food, drink and animal foodstuffs
S14	Keep away from ... (incompatible materials to be indicated by the manufacturer)
S15	Keep away from heat
S16	Keep away from sources of ignition – No smoking
S17	Keep away from combustible material
S18	Handle and open container with care
S20	When using do not eat or drink
S21	When using do not smoke
S22	Do not breathe dust
S23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer)
S24	Avoid contact with skin
S25	Avoid contact with eyes
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S27	Take off immediately all contaminated clothing
S28	After contact with skin, wash immediately with plenty of ... (to be specified by the manufacturer)
S29	Do not empty into drains
S30	Never add water to this product
S33	Take precautionary measures against static discharges
S35	This material and its container must be disposed of in a safe way
S36	Wear suitable protective clothing
S37	Wear suitable gloves

S38	In case of insufficient ventilation wear suitable respiratory equipment
S39	Wear eye/face protection
S40	To clean the floor and all objects contaminated by this material use ... (to be specified by the manufacturer)
S41	In case of fire and/or explosion do not breathe fumes
S42	During fumigation/spraying wear suitable respiratory equipment (appropriate wording to be specified by the manufacturer)
S43	In case of fire use ... (indicate in the space the precise type of fire-fighting equipment. If water increases the risk add - Never use water)
S45	In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
S46	If swallowed, seek medical advice immediately and show this container or label
S47	Keep at temperature not exceeding ... °C (to be specified by the manufacturer)
S48	Keep wet with ... (appropriate material to be specified by the manufacturer)
S49	Keep only in the original container
S50	Do not mix with ... (to be specified by the manufacturer)
S51	Use only in well-ventilated areas
S52	Not recommended for interior use on large surface areas
S53	Avoid exposure - obtain special instructions before use
S56	Dispose of this material and its container at hazardous or special waste collection point
S57	Use appropriate containment to avoid environmental contamination
S59	Refer to manufacturer/supplier for information on recovery/recycling
S60	This material and its container must be disposed of as hazardous waste
S61	Avoid release to the environment. Refer to special instructions/safety data sheet
S62	If swallowed, do not induce vomiting seek medical advice immediately and show this container or label
S63	In case of accident by inhalation: remove casualty to fresh air and keep at rest
S64	If swallowed, rinse mouth with water (only if the person is conscious)

Combinations of S phrases

(S1/2)	Keep locked up and out of the reach of children
S3/7	Keep container tightly closed in a cool place
S3/7/9	Keep container tightly closed in a cool, well-ventilated place
S3/9/14	Keep in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer)

S3/9/14/49	Keep only in the original container in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer)
S3/9/49	Keep only in the original container in a cool, well-ventilated place
S3/14	Keep in a cool place away from ... (incompatible materials to be indicated by the manufacturer)
S7/8	Keep container tightly closed and dry
S7/9	Keep container tightly closed and in a well-ventilated place
S7/47	Keep container tightly closed and at temperature not exceeding ... °C (to be specified by the manufacturer)
S20/21	When using do not eat, drink or smoke
S24/25	Avoid contact with skin and eyes
S27/28	After contact with skin, take off immediately all contaminated clothing, and wash immediately with plenty of ... (to be specified by the manufacturer)
S29/35	Do not empty into drains; dispose of this material and its container in a safe way
S29/56	Do not empty into drains, dispose of this material and its container at hazardous or special waste collection point
S36/37	Wear suitable protective clothing and gloves
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection
S36/39	Wear suitable protective clothing and eye/face protection
S37/39	Wear suitable gloves and eye/face protection
S47/49	Keep only in the original container at temperature not exceeding ... °C (to be specified by the manufacturer)

Annex D

I. Literature relating to safety in chemical labs and hazardous properties of chemical substances

a) General literature relating to workplace safety

Accident insurance providers' document list
Register of accident prevention regulations, rules for security and health protection, data sheets, information relating to all aspects of workplace safety and occupational medicine are issued in regularly updated editions:

a-1 The full set of rules and regulations of the DGUV is to be found at the following internet site:
http://www.dguv.de

Monographs and loose leaf collections

a-2 W. Berthold, U. Löffler:
Lexikon sicherheitstechnischer Begriffe in der Chemie, Verlag Chemie, Weinheim 1981.

a-3 Lexikon Sicherheit und Gesundheit bei der Arbeit, 11. Auflage,
Universum Verlagsanstalt GmbH KG, Wiesbaden 2006.

a-4 W.-D. Ring, H.-Ch. Titze:
Handbuch Deutsches Arbeitsschutzrecht, Ecomed-Verlagsgesellschaft, Landsberg (loose leaf collection).

Teaching material

a-5 DVD
„Alles wird gut", Labor-Sicherheitsfilm der Friedrich-Alexander-University Erlangen-Nürnberg, available from your competent insurance provider, 2006.

a-6 CD-Trainingsprogramm
„Sicheres Arbeiten im Labor",
Berufsgenossenschaft der Chemischen Industrie,
Heidelberg 2005.

a-7 Video-Kassette
„Arbeitsplatz Labor – keine Experimente mit der Sicherheit",
Berufsgenossenschaft der Chemischen Industrie,
Heidelberg 1997.

b) Workplace safety in the chemical laboratory

Information by the accident insurance providers

b-1 „Sicheres Arbeiten in Laboratorien – Grundlagen und Handlungshilfen" (BGI/GUV-I 850-0), available from your competent accident insurance provider.

b-2 „Chemikalienschutzhandschuhe" (BGI/GUV-I 868), available from your competent accident insurance provider.

b-3 „Prüfung ortsveränderlicher elektrischer Betriebsmittel" (GUV-I 8524), available from your compent accident insurance provider.

Monographs and loose leaf collections

b-4 S.G. Luxon:
Hazards in the Chemical Laboratory, Fifth Edition, The Royal Society of Chemistry, London 1992.

b-5 L. Roth, U. Weller:
Sicherheitsfibel Chemie, Ecomed-Verlagsgesellschaft, Landsberg (loose leaf collection).

b-6 H.K. Schäfer, Ch. Jochum:
Sicherheit in der Chemie; Ein Leitfaden für die Praxis, 2. Auflage,
Carl Hanser Verlag, München 1997.

b-7 W. Wolf, H. Schwahn:
Sicherheit im Labor; Einrichten – Experimentieren – Entsorgen,
Diesterweg-Verlag, Frankfurt 1984.

b-8 H. Kruse:
Laborfibel, Wiley-VCH, Weinheim 2002

c) Harmful chemical substances: Information, safe handling and disposal

Legal regulations

c-1 Gesetz zum Schutz vor gefährlichen Stoffen (Chemikaliengesetz – ChemG), Bundesgesetzblatt

c-2 Verordnung zum Schutz vor Gefahrstoffen (Gefahrstoffverordnung – GefStoffV), Bundesgesetzblatt

c-3 Technische Regeln für Gefahrstoffe (TRGS), Gemeinsames Ministerialblatt

Regulations and information by the insurance providers

c-4 Accident prevention regulation „Grundsätze der Prävention“ (BGV/GUV-V A1), available from your competent insurance provider

c-5 Regulation „Umgang mit Gefahrstoffen in Hochschulen“ (GUV-SR 2005), available from your competent insurance provider

c-6 Information „Erste Hilfe bei Einwirken gefährlicher chemischer Stoffe“ (GUV-I 8504), available from your competent accident insurance provider

c-7 „Serie M“ (hazardous substances) data sheets by the Berufsgenossenschaft der Chemischen Industrie, Jedermann-Verlag, Heidelberg.

c-8 Gefahrstoffe 2009,
Universum Verlagsanstalt GmbH KG,
Wiesbaden (issued annually).

CD-ROM

c-9 R. Kühn, K. Birett:
Data sheets for hazardous materials,
Ecomed-Verlagsgesellschaft, Landsberg 2008.

c-10 L. Roth, M. Daunderer:
Poison list, Ecomed-Verlagsgesellschaft, Landsberg.

Loose leaf collections

c-11 G. Sorbe:
Sicherheitstechnische Kenndaten – Gefahrenindex chemischer Stoffe,
Ecomed-Verlagsgesellschaft, Landsberg.

Monographs

c-12 R.J. Lewis:
Sax’s Dangerous Properties of Industrial Materials, 11. Edition and Hawley’s Condensed Chemical Dictionary, 15th Edition, Combination CD, Wiley VCH, Weinheim/Berlin/New York 2009.

c-13 D.B. Walters:
Safe handling of chemical carcinogens, mutagens, teratogens and highly toxic substances,
Ann Arbor Sciences, Ann Arbor, Michigan 1980.

c-14 Deutsche Forschungsgemeinschaft, MAK- und BAT-Werte-Liste 2009, Wiley-VCH, Weinheim/Berlin/New York, issued annually.

d) Hazardous chemical reactions and procedures

Legal regulations and regulations by the accident insurance providers

d-1 Verordnung über Sicherheit und Gesundheitsschutz bei der Bereitstellung von Arbeitsmitteln und deren Benutzung bei der Arbeit, über Sicherheit beim Betrieb überwachungsbedürftiger Anlagen und über die Organisation des betrieblichen Arbeitsschutzes (Betriebssicherheitsverordnung–BetrSichV), available from your bookstore.

d-2 Part 3 „Zentrifugen“ of chapter 2.11 „Betreiben von Maschinen der chemischen Verfahrenstechnik“ of the regulation „Betreiben von Arbeitsmitteln“ (BGR/GUV-R 500), to be obtained exclusively online from http://www.dguv.de

d-3 Regulation „Benutzung von Atemschutzgeräten“ (BGR/GUV-R 190), available from your competent insurance provider.

Other technical literature

d-4 L. Roth, U. Weller: Gefährliche chemische Reaktionen, Ecomed-Verlagsgesellschaft, Landsberg 2004 (CD-ROM).

d-5 P.G. Urben: Bredericks Handbook of reactive chemical hazards, Seventh Edition, Academic Press, Oxford, 2007 (Elsevier Ltd.).

e) Flammable and explosive substances; fire prevention and fire fighting

Legal regulations and regulations by the accident insurance providers

e-1 Verordnung über Sicherheit und Gesundheitsschutz bei der Bereitstellung von Arbeitsmitteln und deren Benutzung bei der Arbeit, über Sicherheit beim Betrieb überwachungsbedürftiger Anlagen und über die Organisation des betrieblichen Arbeitsschutzes (Betriebssicherheitsverordnung–BetrSichV), available from your bookstore.

e-2 „Explosionsschutz-Regeln (EX-RL)“, (BGR/GUV-R 104), available from your competent insurance provider.

e-3 „Richtlinien für die Vermeidung von Zündgefahren infolge elektrostatischer Aufladungen“ (BGR/GUV-R 132), available from your competent insurance provider.

Other technical literature

e-4 G.Rodewald, A. Rempe: Feuerlöschmittel – Eigenschaften, Wirkung, Anwendung, Verlag W. Kohlhammer, Stuttgart 2005.

e-5 K. Nabert, G. Schön: Sicherheitstechnische Kennzahlen brennbarer Gase und Dämpfe, 3. überarbeitete Auflage, zwei Bände mit CD-Rom, Deutscher Eichverlag, Braunschweig 2006.

f) Toxikology of chemicals

Loose leaf collections

f-1 H. Greim: Gesundheitsschädliche Arbeitsstoffe. Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten und Einstufungen, 46. Lieferung, Wiley-VCH, Weinheim/Berlin/New York 2009.

Monographs

f-2 K. Aktories, U. Förstermann, F.B. Hofmann, F. Bernhard: Allgemeine und Spezielle Pharmakologie und Toxikologie, 10. Auflage, Elsevier, München 2005.

f-3 F.-X. Reichl: Taschenatlas Toxikologie, 3. Auflage, Georg-Thieme Verlag, Stuttgart 2009.

g) Disposal

Monographs

g-1 D. Bernabei: Sicherheit – Handbuch für das Labor, GIT-Verlag, Darmstadt 2002.

Loose leaf collections

g-3 L. Roth: Gefahrstoff-Entsorgung, Ecomed-Verlagsgesellschaft, Landsberg.

II. Information on the internet

a) General information relating to workplace safety

a-1 Rules and regulations of the DGUV:
http://www.dguv.de
a-2 Legal regulations and Technical Rules:
http://www.baua.de/prax/index.htm
a-3 „Laboratorien“ by FA Chemie:
http://www.bgrci.de

b) Information on hazardous substances

b-1 GESTIS substance database of the accident insurance providers:
http://www.dguv.de □Webcode: d11892
b-2 Information Office for Safety Data Sheets (Informationsstelle für Sicherheitsdatenblätter, ISI) at the Institut für Arbeitsschutz der DGUV (IFA)
http://www.dguv.de □Webcode: d6130
b-3 Hazardous Substances Information system (Gefahrstoffinformationssystem) of the Berufsgenossenschaft der chemischen Industrie (GisChem):
http://www.gischem.de
b-4 Merck substance database (ChemDAT):
http://www.chemdat.de

Further internet addresses are to be found in the brochure „Gesundheitsschutz beim Umgang mit Gefahrstoffen – PC-Programme und Datenbanken“ (GUV-I 8518) by the DGUV: http://www.dguv.de

Annex E

Immediate measures at the scene of the accident

1 Rescue

- Rescue injured or poisoned persons from the danger zone, paying attention to self-protection.
- Alert the other persons in the danger zone.
- If required, switch off gas, water and electricity, using emergency cut-off if necessary.

2 Request assistance

Enter emergency number / room number / address

First Aider:

Emergency medical service:

Fire brigade:

Poisoning central:

Ophthalmologist:

Surgical ambulance:

To be stated in the emergency call:

Where has it happened?
What has happened?
How many people affected/injured?
Which kinds of injury?
Wait for further enquiry!

3 Provide First Aid

Deutsche Gesetzliche Unfallversicherung (DGUV)

Mittelstraße 51, 10117 Berlin
Tel.: +49 30 288763800
Fax: +49 30 288763808
E-Mail: info@dguv.de
Internet: www.dguv.de

Deutsche Gesetzliche
Unfallversicherung e.V. (DGUV)

Glinkastraße 40
10117 Berlin
Telefon: 030 13001-0 (Zentrale)
E-Mail: info@dguv.de
Internet: www.dguv.de