Safety Rules for Students at the UL FKKT

Second Year

September 2019

CONTENTS

1 INTRODUCTION

During the first year of your studies, you learned about the basic principles of safe work in laboratories. In the second year, the safety training is expanded. You will first briefly repeat the contents of the theoretical part of the first year, i.e.:

- laboratory safety rules,
- use of personal protective equipment,
- laboratory hazards,
- procedures in case of incidents (injury, fire, spillage),
- labelling of hazardous substances,
- activating a handheld fire extinguisher.

In the second year, you will learn more about flammable chemicals and the risks and measures to prevent hazards when working with flammable chemicals. During laboratory work, you will frequently use organic solvents and other volatile compounds whose vapours can be flammable and form explosive mixtures with air. Some organic solvents are also toxic (carcinogenic, teratogenic, mutagenic, toxic to reproduction). With all these hazardous properties in mind, the focus of the health and safety training in the second year will be on safe work with these substances. You will learn about:

- flammable chemicals,
- toxic chemicals,
- respiratory protective equipment.

Classification of hazardous substances

Hazardous chemicals are substances or mixtures that meet the criteria for physical, health or environmental hazards as defined in Annex I to Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006, OJ L 353 of 31 December 2008. According to the Regulation implementing Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (Official Gazette of the Republic of Slovenia, No 56/10) and the Act Amending the Chemicals Act (ZKem-C) (Official Gazette of the Republic of Slovenia, No 9/11), hazardous substances are classified into the following hazard classes:

1. PHYSICAL HAZARDS
2. HEALTH HAZARDS
3. ENVIRONMENTAL HAZARDS

Hazard categories within a hazard class are:

1. PHYSICAL HAZARDS

1.1.	Explosives	**1.9.**	**Pyrophoric liquids**
1.2.	**Flammable gases**	**1.10.**	**Pyrophoric solids**
1.3.	**Flammable aerosols**	**1.11.**	**Self-heating substances and mixtures**
1.4.	Oxidising gases	**1.12.**	**Substances and mixtures which, in contact with water, emit flammable gases**
1.5.	Gases under pressure	1.13.	Oxidising liquids
1.6.	**Flammable liquids**	1.14.	Oxidising solids
1.7.	**Flammable solids**	**1.15.**	**Organic peroxides**
1.8.	**Self-reactive substances and mixtures**	1.16.	Corrosive to metals

2. HEALTH HAZARDS

2.1.	Acute toxicity
2.2.	Skin corrosion/irritation
2.3.	Serious damage to eyes/eye irritation
2.4.	Respiratory or skin sensitisation
2.5.	Germ cell mutagenicity
2.6.	Carcinogenicity
2.7.	Reproductive toxicity
2.8.	Specific target organ toxicity – single exposure – STOT
2.9.	Specific target organ toxicity – repeated exposure – STOT
2.10.	Aspiration hazard

3. ENVIRONMENTAL HAZARDS

3.1.	Hazardous to the aquatic environment – acute
3.2.	Hazardous to the aquatic environment – chronic

2 FLAMMABLE CHEMICALS

Flammable chemicals can easily ignite and form explosive mixtures in contact with the air. The hazard of flammable chemicals is identified by a hazard pictogram:

Flammable chemicals include: flammable gases, flammable aerosols, flammable liquids, flammable solids, self-reactive substances and mixtures, pyrophoric liquids, pyrophoric solids, self-heating substances and mixtures, substances and mixtures which, in contact with water, emit flammable gases, and organic peroxides.

According to the Chemicals Act from 2003, these are divided into three groups:

1. extremely flammable chemicals,
2. highly flammable chemicals,
3. flammable chemicals.

2.1 HAZARDS OF WORKING WITH FLAMMABLE CHEMICALS

The hazards of working with flammable chemicals are:

1. The formation of a gaseous phase (gas, fumes; vapour) which diffuses into the work area and which may be toxic or harmful to health, may cause cancer, mutagenicity, teratogenicity, or may be toxic to reproduction and hazardous to the environment.
2. The uncontrolled release of a liquid flammable chemical into the work area or the environment, contaminating work equipment and surface water, and the concomitant formation of a gaseous phase.
3. Flammable chemicals are very easily ignited and require very little energy to ignite. Fire spreads quickly and easily leads to explosion. A large amount of heat is released. The decomposition products of combustion are toxic, harmful to health and dangerous to the environment.

Preventive measures:

- training for safe work with flammable chemicals,
- removing all possible sources of ignition,
- packaging must be sealed,
- minimum amount of liquids in the workplace,
- using grounding when transferring liquids,
- room must be ventilated and appropriate temperature maintained,
- providing inertisation in closed systems (lowering the concentration of the oxidant),
- using appropriate personal protective equipment,
- written instructions for safe work,
- adequate number of fire extinguishers with suitable fire suppressing agents,

- keeping absorbents close to the work space.

2.1.1 Risks of fire and explosions

A substance can ignite if the following three conditions are met:

1. presence of fuel,
2. presence of an oxidising agent (oxygen),
3. source of ignition.

When working with flammable chemicals, there are almost always two conditions that are met: oxygen and the flammable chemical. For this reason, we need to make sure to avoid the third condition, i.e. the source of ignition, which closes the fire triangle.

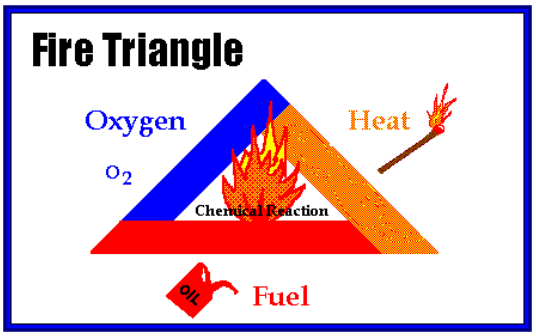

Figure 1: Fire Triangle

Sources of ignition can be classified into four groups:

1. **Mechanical** (friction, metal breaking, hot particles e.g. from grinding or cutting),
2. **Electrical** (electrical wiring, electromagnetic waves, electrostatic voltage, lightning),
3. **Thermal** (hot surfaces, open flames, welding, spontaneous combustion, heat generated by compression),
4. **Chemical** (exothermic reactions, e.g. peroxide decomposition, polymerisation, etc.).

The most important physicochemical data for fire and explosion risk assessment are:

- Vapour pressure – p_r/mbar
- Flash point – T_{pl}/°C
- Flammable or explosive range S_{MV} – Z_{MV}/vol. %
- Boiling point – T_{vr}/°C
- Autoignition temperature – T_{sv}/°C
- Relative density to air
- Relative density to water
- Solubility in water (g/m^3 or g/l)
- Limit values
- Toxicity data – LD_{50}

Flash point of flammable liquids

Flash point is the lowest temperature expressed in °C, at which vapours develop from a liquid or solid in sufficient quantity to ignite when mixed with air if a suitable source of ignition is present above the surface. The vapours are momentarily ignited and extinguished because the substance is not yet heated to a level that would continuously produce a sufficient quantity of the flammable gaseous phase.

Boling point of flammable liquids

The boiling point is the temperature at which the vapour pressure of a liquid reaches 1.013 bar.

The lower the boiling point of a flammable liquid, the earlier an intense fire will start. Liquids with a lower boiling point are therefore more dangerous than liquids with a higher boiling point, even though they have the same flash point.

Autoignition temperature

The autoignition temperature of a flammable substance is the lowest temperature at which the substance in the form of vapour, mist or dust, mixed with air, can ignite or explode without an external source of ignition.

Vapour pressure

Vapour pressure is the equilibrium pressure of saturated vapours above the liquid at a given temperature.

Explosive range

Explosive range is defined by the lower explosive limit (LEL) and the upper explosive limit (UEL) expressed in percentage by volume or g/m^3 of flammable vapours, gases, mist or dust within which combustion, after ignition from an ignition source, propagates independently to a mixture not yet burning (explosion).

Reactivity data

Reactivity data tell us whether a substance is stable (does not react quickly) or reactive (reacts quickly).

Toxicity data

Toxicity data show how likely a substance is to cause biological damage. Toxicity data can be found in safety data sheets.

Data on flash point, boiling point, vapour pressure, autoignition temperature and flammable range for some substances

The table below presents data for ten of the most common flammable chemicals used in the laboratory:

Substance	**Flash point (T_{pl}/°C)**	**Boiling point (T_{vr}/°C)**	**Vapour pressure (p_r/mbar)**	**Autoignition temperature (T_{sv}/°C)**	**Flammable range (vol. %)**
Acetone	-19		240	540	2.5–13
Diethyl ether	-45		585	160	1.9–36
Methanol (CH_3OH)	11 c.c.	64.5	128	455	5.5–11
Ethanol (C_2H_5OH)	12 c.c.	78.3	59	425	3.5–15
Unleaded petrol	< -40	25–215	350–900	250–460	0.6–8
Diesel fuel	> 55	160–385	–	> 200	0.6–6.5
Benzene (C_6H_6)	-11	80.1	101	555	1.4–8
Styrene ($C_6H_5CH=CH_2$)	31	145	6	480	1.1–8.9
Aniline ($C_6H_5NH_2$)	76	77	0.5	540	1.3–11
Dimethyl sulphide $(CH_3)_2S$	-37	37	645	205	2.2–9.7

Hazards of static electricity

When handling flammable chemicals, there is a risk that the mixture of vapours, gases and dust with air could ignite and explode due to static electricity. Electrostatic charges are discharged by a spark or a train of sparks which have sufficient energy to cause the flammable mixture to explode.

Electrostatic charges are produced in objects by the influence of mechanical action such as lifting, crushing, transferring liquids, mixing, pouring, etc. The specific resistance of the substance, the specific electrical conductivity and the surface resistance are important in electrostatic charges. Conductive materials have a specific resistance of less than 10^6 Ω Liquids with specific resistance greater than 10^{10} Ω and solids with resistance greater than 10^9 Ω can be easily charged with electrostatic energy.

The generation of static electricity can be avoided by:

- grounding of conductive parts (yellow-green wire),
- conductive flooring,
- conductive footwear and clothing made of cotton,
- grounding the containers for transferring flammable chemicals,
- using Ex-proof electrical installation,
- and other measures.

Incompatibility of substances

As we use different chemicals in the laboratory, sooner or later we will come into contact with substances that are incompatible. Mixing incompatible chemicals can lead to explosions or the formation of highly toxic or flammable substances. HCN (hydrogen cyanide), for example, is incompatible with acids and bases. It forms highly toxic fumes with acids and reacts aggressively with bases.

Strong oxidising and reducing agents are also incompatible, but pose a serious hazard even when mixed with chemicals that are not such strong reducing or oxidising agents. The hazard level depends on the quantity of the substance, so that in the laboratory the hazard is lower because the quantities are also smaller, whereas for larger quantities (over 500 g or 1 l) adequate, separate storage is required.

A table of some incompatible substances for laboratory chemicals is given in Appendix 1.

2.1.2 Health hazards in working with flammable chemicals

Some flammable chemicals may be hazardous to health if their vapours or fumes are inhaled. In addition to being classified as flammable, chemicals may have one of the following properties:

- toxicity,
- carcinogenicity,
- mutagenicity,
- reproductive toxicity.

These health hazards of working with flammable chemicals are given in Sections 3 and 4.

Properties of organic solvents

An organic solvent is any volatile organic compound used alone or in combination with other substances, which does not undergo any chemical change, having the power to dissolve raw materials, products or waste materials, or used as a cleaning agent for dissolving impurities, as a dissolving agent, as a dispersing medium, as a viscosity or surface tension control agent, as a plasticiser, or as a protective agent.

Organic solvents can enter the body through the following routes:

1. through the lungs (inhalation),
2. through the skin (absorption),
3. through the gastrointestinal tract (ingestion).

The most common route of entry of organic solvents into the body is by inhalation. The amount of solvents depends on the concentration, the time of exposure and the difficulty of the work or the rate of breathing. The effects of organic solvents on our body can be specific or non-specific.

a) Non-specific effects
dissolve fat (in contact with skin, they dissolve the fat layer of the skin, thus lowering the skin's resistance and pH)
- Systemic effect, manifested as depression of the central nervous system (narcotic effect: first drunkenness, followed by euphoria, drowsiness, narcosis, coma and death).
- Immediate effect due to local irritation, mainly of the upper respiratory tract (sometimes also of the lower respiratory tract), which may also lead to pulmonary oedema.
- We can get used to some of these effects. The effects are added up, and frequently multiplied.
- Chronic exposure causes fatigue, irritability, headache and insomnia.

b) Specific effects
can be latent, and appear several hours or days after ingestion or inhalation of the substance due to the formation of toxic metabolites. The presence of organic solvents in the body affects the haematopoietic organs, the nervous system, liver, kidneys, heart, and the metabolism of fats and carbohydrates. Latent specific effects are carcinogenic (benzene and its derivatives, aniline), mutagenic or harmful to the foetus (see Section 3).
As organic solvents are generally flammable and explosive, they pose a potential risk of fire and accidents at work. Organic solvents are typically volatile and their vapours are heavier than air, so they accumulate at ground level, which should be considered when planning ventilation in the work environment. The vapours of organic solvents must be contained at the source by an extraction system

2.2 SAFETY MEASURES FOR HANDLING FLAMMABLE CHEMICALS

The following general safety measures must be observed when handling flammable liquids:

1. Make sure that the room is well ventilated. Depending on the relative density of the vapours, extract air from the lower or upper part of the room.
2. Apply safety measures for protection against static electricity.
3. The floors must be solvent-resistant, waterproof and conductive.
4. Electrical instruments must be grounded.
5. Fire extinguishing agents must be provided in all laboratories.
6. Vapours must be extracted at the source of release.
7. Containers with flammable liquids must be tightly sealed
8. Only the minimum quantities necessary for the work may be kept at the workstations.
9. Flammable liquids must be stored in special metal cabinets for the storage of flammable liquids. The cabinets must be ventilated.
10. All sources of ignition must be prevented. Smoking and welding are strictly prohibited.
11. Observe the safety and technical data in the safety data sheets and the labels on the packaging.
12. Use personal protective equipment.

3 TOXIC CHEMICALS

"Only the dose makes a poison." Paracelsus (1493–1541)


Figure 2: Auroleus Phillipus Theostratus Bombastus von Hohenheim – Paracelsus, (11 November or 17 December 1493, Einsiedeln, Switzerland; 24 September 1541, Salzburg)

3.1 PROPERTIES OF TOXIC CHEMICALS

A **TOXIN** is any substance that is harmful to the human body if it reaches the surface of the body or is introduced into it. Depending on the quantity or its composition, a toxic substance disrupts the functioning of the body and affects its anatomic structure. Toxic substances have an immediate (acute toxicity) or a delayed effect (chronic toxicity). They have a general or a local effect on the body

HARMFUL SUBSTANCES are those which, during manufacture, transport, storage or use, escape or are formed, thus causing infectious, irritating, suffocating, toxic or other harmful effects: dust, smoke, gas, mist, fumes, vapours, or fibres in quantities that can affect the health of persons coming into contact with them.

TOXICOLOGY is the discipline that studies the harmful effects of pure chemicals or their mixtures on living organisms. Toxicology involves the study of interactions between chemical and biological systems in order to quantify the potential for harmful effects on intact living organisms and investigates the nature, effects, mechanisms and reversibility of harmful effects.

The **TOXICITY** of a substance is its capacity to cause biological damage.

Toxic chemicals can enter the body through the following routes:

- inhalation,
- ingestion,
- contact with the skin or eyes,
- injection.

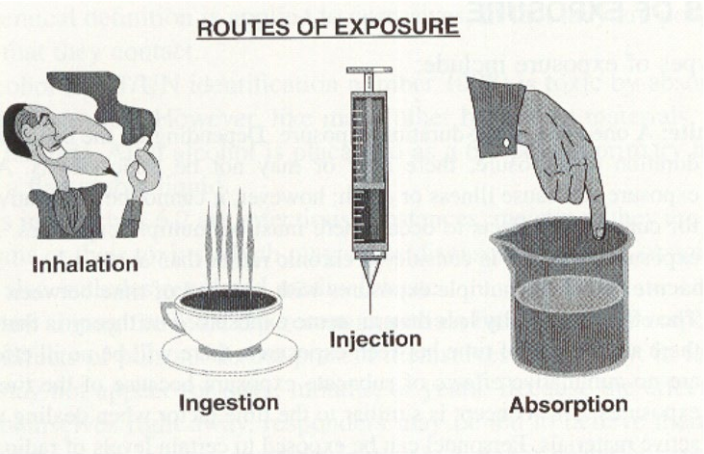

Figure 3: Routes of exposure

The **LD_{50}** value (lethal dose) is the amount of a substance (mg substance/kg body weight) that causes death or mortality of 50% of the test specimens within 14 days.

The **LC_{50}** value (lethal concentration) is the concentration of the substance (mg or cm^3 of substance/m^3) that causes death or mortality of 50% of the test specimens within 14 days.

Table 1: LD_{50} values for some chemicals

Substance	**LD_{50}/mg/kg**
Sugar	29,000
Ethyl alcohol	14,000
Sodium chloride	3,000
Vitamin A	2,000
Aspirin	1,000
Caffeine	192
Sodium nitrate	85
Nicotine	53
Sodium cyanide	6.4
Strychnine	2.5

The way the substance can enter the body depends on its state of matter. Gases normally enter the body through the respiratory tract. Liquids act primarily on the skin, either by eroding it, dissolving fat, causing eczema, or penetrating into the body though the skin. In the form of vapours and aerosols, they also enter the body through the respiratory tract and may affect the eyes. Solids may enter through ingestion, and if in the form of fine dust particles, may also enter through inhalation.

The level of health damage depends on the following factors:

1. chemical composition of the substance,
2. concentration of the substance,
3. period of exposure.

The concentrations of substances in air at the workplace at which no harmful health effects are normally expected in exposed workers are expressed by threshold limit values for occupational exposure.

TLV – threshold limit value for occupational exposure

THRESHOLD LIMIT VALUE (**TLV-TWA**) for occupational exposure means the average concentration of a hazardous chemical substance in the air at the workplace within the inhalation zone which is generally not harmful to the health of the worker if the worker works at a concentration of the hazardous chemical substance in the air, which is lower than or equal to the threshold limit value for the hazardous chemical substance, for 8 hours a day, or 40 hours a week, for the whole period of service, under normal microclimatic conditions (20 °C and $1.013 \cdot 10^5$ Pa) while doing physically light work. It is expressed in ml/m^3 (ppm) or mg/m^3.

SHORT-TERM EXPOSURE LIMIT (**TLV-STEL**) means the permissible upward deviation from the limit value of a hazardous substance for short periods of time, or the factor by which the limit value is multiplied to give the concentration of a substance to which a worker can be exposed for a short period of time without health risk. Short-term exposure may last no more than 15 minutes and may not be repeated more than four times in a working shift, and there must be a minimum of 60 minute interval between two exposures to that concentration. It is expressed in ml/m^3 (ppm) or mg/m^3.

TECHNICALLY ACHIEVABLE CONCENTRATION (**TAC**) is the concentration of a substance at the workplace which, in the light of the state of the art, is achievable and still tolerable and which must be considered as a criterion for appropriate safety measures and technical measurement control at the workplace. The TAC only applies to carcinogens where it is not possible to set reasonable limit values for the workplace. The TAC is meant to reduce the risk of health damage, but cannot completely eliminate it.

*Table 2: List of some volatile organic substances with TLV and TLV-STEL values**

Chemical name	TLV (mg/m^3)	TLV-STEL*	Group of carcinogens
ACETONE	1,210		
DIETHYL ETHER	308	2	
BENZENE	3.25	4	1
ETHANOL	1,900	4	
METHANOL	260		
DICHLOROMETHANE	350	4	2

TLV-STEL* is a factor by which we multiply the TLV value

BIOLOGICAL LIMIT VALUE (**BLV**) means the threshold level of a hazardous chemical substance and its metabolites in tissues, body fluids or exhaled air, regardless of whether the hazardous chemical substance is introduced into the body by inhalation, ingestion or dermal uptake.

3.2 CLASSIFICATION OF TOXIC SUBSTANCES

Hazardous chemicals are substances or mixtures that meet the criteria for physical, health or environmental hazards as defined in Annex I to Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006, OJ L 353 of 31 December 2008. According to the Regulation implementing Regulation No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (Official Gazette of the Republic of Slovenia, No 56/10) and the Act Amending the Chemicals Act (ZKem-C) (Official Gazette of the Republic of Slovenia, No 9/11), hazardous substances are classified into the following hazard classes:

1. PHYSICAL HAZARDS
2. HEALTH HAZARDS
3. ENVIRONMENTAL HAZARDS

Hazard categories within the health hazard class are:

2.1.	Acute toxicity
2.2.	Skin corrosion/irritation
2.3.	Serious damage to eyes/eye irritation
2.4.	Respiratory or skin sensitisation
2.5.	Germ cell mutagenicity
2.6.	Carcinogenicity
2.7.	Reproductive toxicity
2.8.	Specific target organ toxicity – single exposure – STOT
2.9.	Specific target organ toxicity – repeated exposure – STOT
2.10.	Aspiration hazard

According to the Chemicals Act from 2003, toxic chemicals are divided into three groups:

1. highly toxic chemicals,
2. toxic chemicals,
3. harmful chemicals.

	LD_{50} values for poisoning by ingestion mg/kg	**LD_{50} values for poisoning through the skin mg/kg**	**LC_{50} values for poisoning by inhalation mg/l (4 hrs)**
Highly toxic	< 25	< 50	< 0.5
Toxic	25–200	50–400	0.5–2
Harmful	200–2000	400–2000	2–20

3.3 LABELLING OF TOXIC SUBSTANCES

Toxic chemicals are identified by the following hazard pictograms:

Hazard pictogram	Hazard
	Acute toxicity (oral, dermal, inhalation).
	Skin corrosion Serious eye damage
	Respiratory sensitisation Germ cell mutagenicity Carcinogenicity Reproductive toxicity Specific target organ toxicity – single exposure Specific target organ toxicity – repeated exposure Aspiration hazard
	Acute toxicity (oral, dermal, inhalation). Skin irritation Eye irritation Skin sensitisation Specific target organ toxicity – single exposure Respiratory tract irritation Narcotic effects

According to the Chemicals Act from 2003, they are labelled with the following symbols:

The following chemicals are also classified as toxic:

1. carcinogens,
2. mutagens,
3. reproductive toxicants.

3.3.1 Carcinogens

A carcinogen is a substance or a mixture of substances which induce cancer or increase its incidence. Substances which have induced benign and malignant tumours in well performed experimental studies on animals are also considered to be presumed or suspected human carcinogens unless there is strong evidence that the mechanism of tumour formation is not relevant for humans.

For the purpose of classification for carcinogenicity, substances are allocated to one of two categories based on strength of evidence and additional considerations (weight of evidence). In certain instances, route-specific classification may be warranted, if it can be conclusively proved that no other route of exposure exhibits the hazard.

Category	Criterion
1	Known or presumed human carcinogens. A substance is classified in Category 1 for carcinogenicity on the basis of epidemiological and/or animal data. A substance may also be included in category 1A if it is known that it is a human carcinogen, based on the existence of human testing.
1A 1B	Category 1B: if it is supposed to be a human carcinogen, based on the existence of animal testing. The classification in Category 1A and 1B is based on the strength of evidence together with additional considerations. This evidence may come from: • human studies that establish a causal relationship between human exposure to a substance and the development of cancer (known human carcinogen); or • animal experiments for which there is sufficient evidence to demonstrate animal carcinogenicity (presumed human carcinogen). In addition, on a case-by-case basis, scientific judgment may warrant a decision of presumed human carcinogenicity derived from studies showing limited evidence of carcinogenicity in humans together with limited evidence of carcinogenicity in experimental animals.
2	Suspected human carcinogens. The placing of a substance in Category 2 is done on the basis of evidence obtained from human and/or animal studies, but which is not sufficiently convincing to place the substance in Category 1A or 1B, based on strength of evidence together with additional considerations. Such evidence may be derived either from limited evidence of carcinogenicity in human studies or from limited evidence of carcinogenicity in animal studies.

3.3.2 Mutagens

Mutation is a permanent change in the amount or structure of the genetic material in a cell. The term 'mutation' applies both to heritable genetic changes that may be manifested at the phenotypic level and to the underlying DNA modifications when known (including specific base pair changes and chromosomal translocations). The term 'mutagenic' and 'mutagen' will be used for agents giving rise to an increased occurrence of mutations in populations of cells and/or organisms.

The more general terms 'genotoxic' and 'genotoxicity' apply to agents or processes which alter the structure, information content, or segregation of DNA, including those which cause DNA damage by interfering with normal replication processes, or which in a non-physiological manner (temporarily) alter its replication.

Genotoxicity test results are usually taken as indicators for mutagenic effects.

Hazard categories for germ cell mutagens

Category	Criterion
1	Substances known to induce heritable mutations or to be regarded as if they induce heritable mutations in the germ cells of humans. Substances known to induce heritable mutations in the germ cells of humans.
1A	The classification in Category 1A is based on positive evidence from human epidemiological studies. Substances to be regarded as if they induce heritable mutations in the germ cells of humans.
1B	The classification in Category 1B is based on: • positive result(s) from in vivo heritable germ cell mutagenicity tests in mammals; or • positive result(s) from in vivo somatic cell mutagenicity tests in mammals, in combination with some evidence that the substance has potential to cause mutations to germ cells. It is possible to derive this supporting evidence from mutagenicity/genotoxicity tests in germ cells in vivo, or by demonstrating the ability of the substance or its metabolite(s) to interact with the genetic material of germ cells; or • positive results from tests showing mutagenic effects in the germ cells of humans, without demonstration of transmission to progeny; for example, an increase in the frequency of aneuploidy in sperm cells of exposed people.
2	Substances which cause concern for humans owing to the possibility that they may induce heritable mutations in the germ cells of humans. The classification in Category 2 is based on: • positive evidence obtained from experiments in mammals and/or in some cases from in vitro experiments, obtained from: • somatic cell mutagenicity tests in vivo, in mammals; or • other in vivo somatic cell genotoxicity tests which are supported by positive results from in vitro mutagenicity assays. Note: Substances which are positive in invitro mammalian mutagenicity assays, and which also show chemical structure activity relationship to known germ cell mutagens, shall be considered for classification as Category 2 mutagens.

3.3.3 Reproductive toxicants

Reproductive toxicity includes impairment of male and female reproductive functions or capacity and the induction of non-inheritable harmful effects on the progeny. This may be classified under two main headings:

1. Effects on male or female fertility
2. Developmental toxicity, is taken in its widest sense to include any effect interfering with normal development, both before and after birth.

Reproductive toxicity includes adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring.

In this classification system, reproductive toxicity is subdivided under two main headings:

a) adverse effects on sexual function and fertility,
b) adverse effects on development of the offspring.

Some reproductive toxic effects cannot be clearly assigned to either impairment of sexual function and fertility or to developmental toxicity. Nonetheless, substances with these effects, or mixtures containing them, shall be classified as reproductive toxicants.

For the purpose of classification, the hazard class Reproductive Toxicity is differentiated into

- adverse effects
- on sexual function and fertility, or
- on development,
- effects on or via lactation.

Hazard categories for reproductive toxicants

Category	Criterion
1	Known or presumed human reproductive toxicant. Substances are classified in Category 1 for reproductive toxicity when they are known to have produced an adverse effect on sexual function and fertility, or on development in humans or when there is evidence from animal studies, possibly supplemented with other information, to provide a strong presumption that the substance has the capacity to interfere with reproduction in humans. The classification of a substance is further distinguished on the basis of whether the evidence for classification is primarily from human data (Category 1A) or from animal data (Category 1B).
1A	Known human reproductive toxicant. The classification of a substance in Category 1A is largely based on evidence from humans.
1B	Presumed human reproductive toxicant. The classification of a substance in Category 1B is largely based on data from animal studies. Such data shall provide clear evidence of an adverse effect on sexual function and fertility or on development in the absence of other toxic effects, or if occurring together with other toxic effects the adverse effect on reproduction is considered not to be a secondary non-specific consequence of other toxic effects. However, when there is mechanistic information that raises doubt about the relevance of the effect for humans, classification in Category 2 may be more appropriate.
2	Suspected human reproductive toxicant. Substances are classified in Category 2 for reproductive toxicity when there is some evidence from humans or experimental animals, possibly supplemented with other information, of an adverse effect on sexual function and fertility, or on development, and where the evidence is not sufficiently convincing to place the substance in Category 1. If deficiencies in the study make the quality of evidence less convincing, Category 2 could be the more appropriate classification. Such effects shall have been observed in the absence of other toxic effects, or if occurring together with other toxic effects the adverse effect on reproduction is considered not to be a secondary non-specific consequence of the other toxic effects.

3.3.4 Safety measures for working with carcinogens, mutagens and reproductive toxicants (CMR substances)

1. Replacing CMR substances with other non-hazardous or less hazardous ones.
2. Selecting less hazardous technological processes (e.g. transform carcinogenic solids in powder form into suspensions or granules).
3. Measuring concentrations of substances in the workplace.
4. Safety instructions clearly displayed in the workplace. They must show the hazardous effects of CMR substances and the measures needed to protect against them.
5. All work in the laboratory must be carried out in a fume hood or in closed devices.
6. Persons handling CMR substances must be instructed on the hazardous effects of exposure to these chemicals and on the measures necessary to protect against them.
7. Stricter hygiene regime.

8. Carrying out medical examinations of people handling CMR substances.
9. Pregnant women and persons under 18 years of age must not handle CMR substances.

4 RESPIRATORY PROTECTIVE EQUIPMENT

Breathing is a process that is essential for life. The body's cells need oxygen to live. Oxygen is supplied to our body from the air through the process of breathing. Inhaling brings fresh air into the lungs and allows the exchange of oxygen and carbon dioxide. In this process, oxygen is transferred from the inhaled air to the oxygen carriers in the blood, and the inhaled air is simultaneously enriched with carbon dioxide transferred from the blood. Carbon dioxide is a product of cellular respiration. Thus, when exhaling, the concentration of oxygen in the exhaled air is lower and the concentration of carbon dioxide is higher. The numerical values of the concentrations are shown in Figure 5, which shows the average composition of inhaled and exhaled air. Inhaled air contains 78% of nitrogen, which is an inert gas from the view point of breathing. Inhaled air also contains about 21% of oxygen and 0.04% of carbon dioxide. Exhaled air contains on average about 17% of oxygen and 4% of carbon dioxide. Exhaled air is usually also more humid.

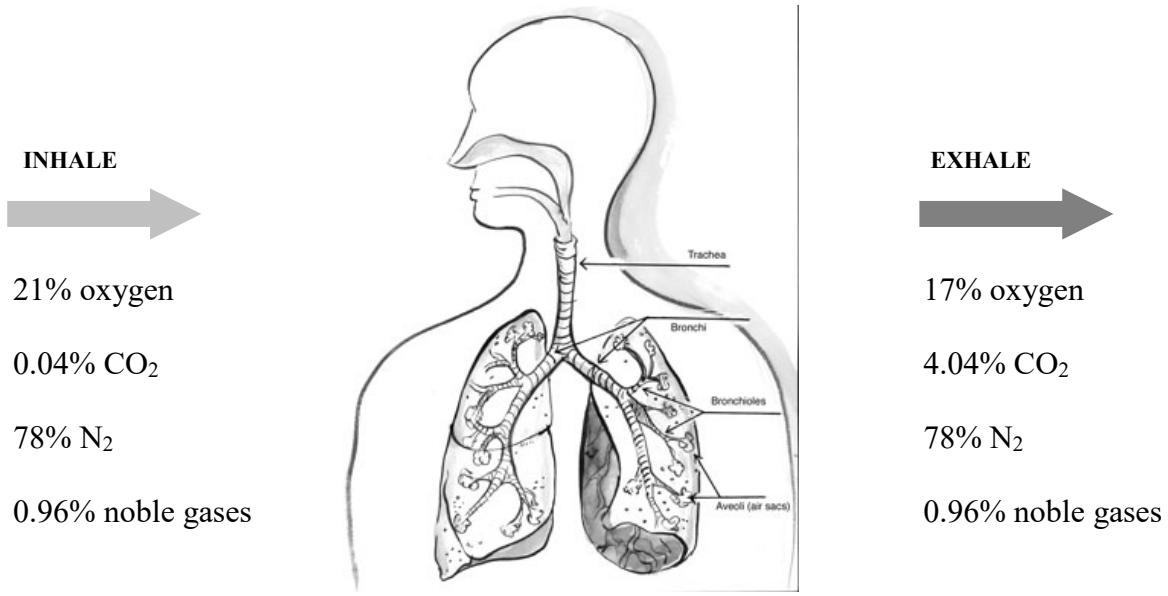

Figure 4: Schematic illustration of the airways and the composition of inhaled and exhaled air

If there are harmful substances present in the air, or if their concentration is higher than the permissible limit value (LV), we are talking about air contamination and we need to protect our respiratory system. The following four steps are important for respiratory protection:

Hazard identification

Before selecting the appropriate respiratory protective equipment, it is necessary to know the state of matter or type of the harmful substance to protect against. Substances harmful to the respiratory system may be in the form of dust, smoke, mist or gas. Oxygen deficiency in the air or extremely low or high air temperatures can also be very dangerous.

Health effects of harmful substances

Once the harmful substances have been identified, their adverse health effects must be identified and assessed. This information is also important in terms of better motivation to actually use and wear personal protective equipment.

Choosing the right respiratory protection
There are several types of respiratory protective equipment with very different effects and applications. The most universal personal protective equipment for respiratory protection is the self-contained breathing apparatus (SCBA). However, such a high level of respiratory protection is mostly not necessary for normal work and would be an undue hindrance to work. A suitable filtering system with a mask or filter to protect against particles, aerosols, gases, vapours, etc. is usually sufficient. However, when selecting personal protective equipment with air filtration, it is of course necessary to pay attention to the specific purpose of use (harmful substance), as otherwise there may be no protection or the protection will be inadequate.

Education and training in the use of the selected personal protective equipment
Users must be able to select the appropriate equipment to protect their respiratory system and also be able to use it correctly and diligently. It is therefore important that users are trained in the correct fitting of the equipment to the face, its use and also its maintenance. It is also essential to regularly check the tightness of the respiratory protective equipment before entering a hazardous area, as this verifies the adequacy of the protection.

In terms of oxygen circulation, personal protective equipment for respiratory protection can be classified into open-circuit, semi-open-circuit and closed-circuit equipment. In the first case, breathing air is taken directly from the surroundings to which the exhaled air is returned. In the second case, breathing air is taken from a pressure vessel or container where oxygen is produced via a chemical process and the exhaled air is released to the surroundings. In the case of a closed circuit, the exhaled air is returned to the system, but is partially purified by an appropriate process before being inhaled again. The latter principle prolongs the autonomy of the breathing apparatus.

Respiratory protective equipment can also be classified according to its mode of operation, i.e. into air-purifying systems using filtration and self-contained respiratory systems that supply air or oxygen from an uncontaminated source.

4.1 FILTERING DEVICES

Filtering systems for respiratory protection are only useful when the air contains at least 17 percent oxygen by volume and the concentration of the contaminant is not too high (usually up to 1 percent by volume). They work on the principle of filtration, whereby the inhaled air first passes through a filter that removes contaminants. Filtration can be achieved by different mechanisms, as shown for example in Figure 6. These mechanisms are as follows:

- *Gravity sedimentation* – larger particles (usually over 2 mm) are trapped in the filter by gravity.
- *Inertial impaction* – this is inertial capture that usually occurs with particles between 0.5 and 2 mm in size. This is because due to inertia, they cannot follow the curved path of the gas between the fibres of the filter, so sooner or later they collide with the fibre and become trapped.
- *Direct interception* – particles between 0.05 and 0.5 mm can follow the gas path between the filter fibres, but may still touch and stick to the fibre.
- *Diffusion* – smaller particles (typically below 0.1 mm) may collide with and be trapped in the fibre due to diffusion in the gas stream.
- *Electrostatic attraction* – charged particles hit the fibre due to electrostatic attraction and are captured by the fibre.

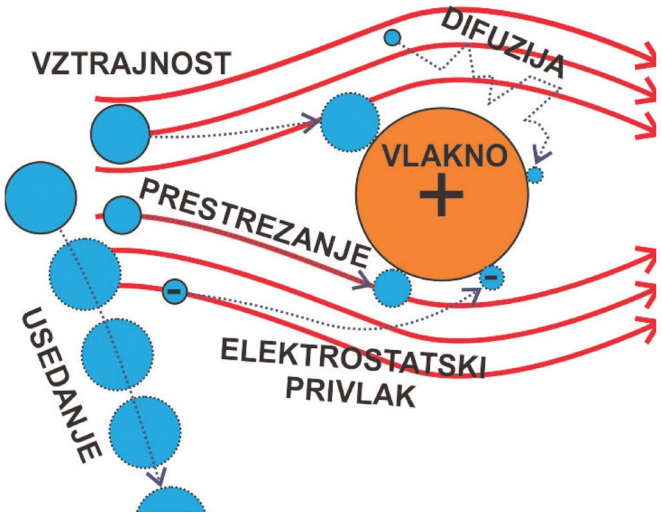

Figure 5: Schematic illustration of the different filtration mechanisms

The filters in respiratory protective equipment are usually multi-layered to prevent rapid clogging and may use one or a combination of several mechanisms. We can thus speak of:

- *Mechanical filters* that use mechanical filtration. Their efficiency depends on the number of fibres in the filter that trap dust particles. Unfortunately, however, a higher amount of filler also means a higher breathing resistance.
- *Electrostatic filters* that contain statically charged fibres. Such fibres attract charged dust particles, so less filler is needed to achieve the same efficiency as in mechanical filtration.
- *Combined filters* – a combination of mechanical and electrostatic filters is needed when dust particles are not necessarily charged, e.g. oil aerosols. These are usually very efficient filters and their breathing resistance is not high.

4.1.1 Differentiation of filtering devices

Depending on the type of the contaminant, filtering devices can be classified into filters for protection against particles, filters for protection against gases and vapours, and filters for protection against particles, gases and vapours, as shown in the diagram in Figure 6.

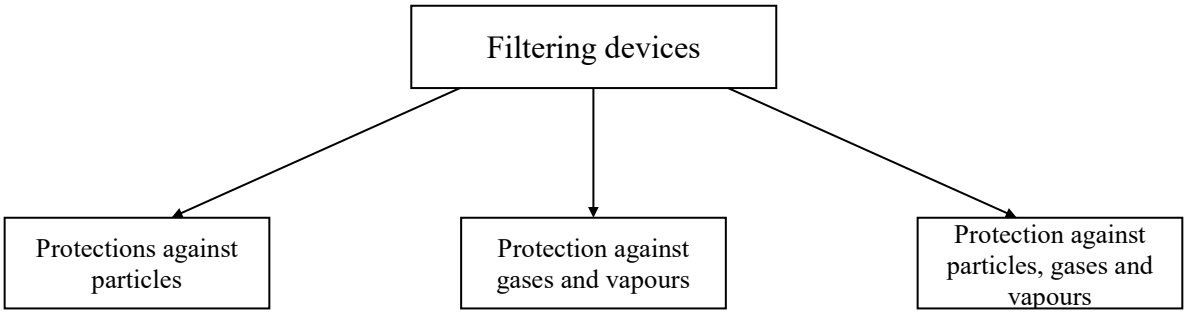

Figure 6: Differentiation of filtering devices with regard to the type of the contaminant

According to the way they are used, they are classified into respirators and face masks. Respirators have a filter in the form of a face mask, as shown in Figure 7, through which air is both inhaled and exhaled.

Figure 7: A standard respirator

Examples of full-face and half-face masks are shown in Figure 8. A full face mask covers the mouth, nose, chin and eyes and also contains an inner mask to direct the air and prevent the mask from fogging up from the inside. A half-face mask covers only the mouth, nose and chin, and there are also versions with only a mouthpiece with a filter and a nose clip.

Figure 8: A full-face and a half-face mask

4.1.2 Selecting the right filtering device

When deciding on the type of the filtering device, we need to consider the state of matter of the contaminant (dust, gases, vapours), the type of the contaminant, and the concentration of the contaminant (based on measurements of contaminant concentration in the air) The most important consideration in the selection of the appropriate filtering device should be the filter. Combined protection against particles, vapours and gases is achieved by a combination of a mechanical filter that stops particles (dust and aerosols) and an active filler that can absorb toxic vapours and gases. Table 3 shows the characteristic properties of filters according to the type of the contaminant and the level of capture capacity.

Table 3: Characteristics of different filter classes

	Filter class	Protection against	Maximum allowable contaminant concentration
Filter for the protection against gases		gases, vapours	
		Capacity:	
	1	low	0.1 vol % (1000 ppm)
	2	medium	0.5 vol % (5000 ppm)
	3	High	1.0 vol % (10000 ppm)
Filter for the protection against particles		particles	
		Capacity:	
	1	low	4 x exceeded LV
	2	medium	12 x exceeded LV
	3	High	25 x exceeded LV
Combined filter	e.g.:	gases, vapours and particles	
	1 - P2		
	2 - P2		values depend on the combination
	2 - P3		
	3 - P3		

Filters for protection against vapours and gases are colour-coded with the colour printed on the side of the filter to indicate the type of the contaminant (gas or vapour). The meaning of each colour and the corresponding designation is explained in Table 4.

Table 4: Filter colour codes

Colour	Filter type	Typical application
Brown	AX	Gases and vapours of organic compounds. Boiling point under 65 °C
Brown	A	Gases and vapours of organic compounds. Boiling point above 65 °C
Grey	B	Inorganic gases and vapours, e.g. chlorine, hydrogen sulphite, hydrogen cyanide
Yellow	E	Hydrogen chloride, sulphur dioxide
Green	K	Ammonia and its derivatives
Black	CE	Carbon monoxide
Red	Hg	Mercury vapour
Blue	NO	Nitrous gases (including nitrogen monoxide)
White	P	Particles

4.2 BREATHING APPARATUSES

Breathing apparatus must be used instead of filtering devices if:

- the oxygen content of the room is lower than 17 percent by volume,
- we are in poorly ventilated areas such as tanks, reservoirs, tunnels, etc,
- the concentration of harmful substances is unknown,
- the concentration of harmful substances is higher than the capacity of the filtering devices,
- we are dealing with harmful substances that have poor warning signals such as unpleasant smell, taste or other irritating effects (e.g. aniline, benzene, hexane, methyl chloride, methanol, formic acid).

Depending on the air supply, breathing apparatuses are divided into fresh air hose breathing apparatuses (FAHBA), where the air is supplied through an air hose, and self-contained breathing apparatuses (SCBA), which have their own air tank. In the case of fresh air hose breathing apparatuses, air may be supplied by a pump or compressed air may be supplied, as shown in Figure 9. Figure 10 shows an SCBA supplied with air from its own source (tank).

Figure 9: Fresh air hose breathing apparatus

Figure 10: A self-contained breathing apparatus

5 LIST OF REFERENCES

1. Regulation No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006
2. Chemicals Act (Official Gazette of the Republic of Slovenia No. 110/2003.)
3. Practical guidelines for working with hazardous chemical substances (Official Gazette of the Republic of Slovenia No. 50/03, 78/18)
4. Rules on the protection of workers from risks related to exposure to chemical agents at work (Official Gazette of the Republic of Slovenia, No. 100/01, 39/05, 53/07, 102/10, 43/11 – ZVZD-1, 38/15 and 78/18)
5. Prudent Practices in the Laboratory, National Research Council, USA, 1995
6. Robert Burke: Hazardous Materials Chemistry for Emergency Responders, USA 1997
7. SIST EN 132 Respiratory protective devices – Definitions of terms and pictograms
8. SIST EN 133 Respiratory protective devices – Classification
9. Catalogues of manufacturers of respiratory protective equipment Dräger and 3M
10. Decree on the limit values for atmospheric emissions of volatile organic compounds from installations using organic solvents (Official Gazette of the Republic of Slovenia No. 35/15 and 58/16)

Appendix 1: Table of incompatible chemicals

The substances in the left-hand column must not come into contact with the substances in the right-hand column under uncontrolled conditions.

Acetic acid	Peroxides, permanganates, chromium (VI) compounds, nitric acid
Acetic anhydride	Hydroxyl-containing compounds such as ethylene glycol, perchloric acid
Acetone	Concentrated nitric and sulphuric acid mixtures, hydrogen peroxide
Acetylene	Chlorine, bromine, copper, silver, fluorine, mercury
Sodium, potassium, powdered aluminium	CO_2, CCl_4, other chlorinated hydrocarbons (prohibit the use of water, foam, and dry chemical extinguishers on fires involving these metals – dry sand should be employed)
Ammonia	Mercury, chlorine, calcium hypochlorite, iodine, bromine, hydrogen fluoride
Ammonium nitrate	Acids, metal powders, flammable liquids, chlorates, nitrates, sulphur, finely divided organics, combustibles
Aniline	Nitric acid, hydrogen peroxide
Bromine	Ammonia, acetylene, butadiene, petroleum gases, sodium carbide, turpentine, benzene, finely divided metals
Calcium oxide	Water
Carbon, activated	Calcium hypochlorite, other oxidants
Chlorates	Ammonium salts, acids, metal powders, sulphur, finely divided organics, combustibles
Chromium (VI) compounds	Acetic acid, naphthalene, camphor, glycerol, turpentine, benzene, metal powders
Chlorine	Ammonia, acetylene, butadiene, butane, other petroleum gases, hydrogen, sodium carbide, turpentine, benzene, metal powders
Chlorine dioxide	Ammonia, methane, phosphorus, hydrogen sulphide
Copper	Acetylene, hydrogen peroxide
Fluorine	Isolate from everything
Hydrazine	Hydrogen peroxide, nitric acid, all oxidants
Hydrocarbons (benzene, butane, propane, gasoline, turpentine, etc.)	Fluorine, chlorine, bromine, chromic acid, peroxides
Hydrocyanic acid	Nitric acid, alkalis

Hydrofluoric acid (anhydrous), hydrogen fluoride	Ammonia
Hydrogen sulphide	Fuming nitric acid, oxidising gases
Iodine	Acetylene, ammonia
Mercury	Acetylene, fulminic acid (product of a mixture of nitric acid and ethanol), ammonia
Nitric acid, concentrated	Acetic acid, acetone, alcohol, aniline, chromic acid, hydrocyanic acid, hydrogen sulphide, flammable liquids and gases, nitrates
Nitroparaffins	Inorganic bases, amines
Oxalic acid	Silver and mercury and their salts
Oxygen	Oils, grease, hydrogen, flammable liquids, gases and solids
Perchloric acid	Bismuth and its alloys, alcohol, paper, wood, grease, oils, (organics)
Peroxides, organic	Acids (organic or mineral), (also avoid friction, store cold)
Phosphorus (white)	Air, oxygen
Phosphorus pentoxide	Alcohols, strong bases, water
Potassium chlorate	Acids (see also chlorates)
Potassium perchlorate	Acids (see also perchloric acid)
Potassium permanganate	Glycerol, ethylene glycol, sulphuric acid, benzaldehyde
Silver and silver salts	Acetylene, oxalic acid, tartaric acid, fulminic acid, (formed from a mixture of nitric acid and ethanol), ammonium compounds
Sodium nitrite	Ammonium nitrate, ammonia salts
Sodium peroxide	Any oxidant, ethanol, methanol, glacial acetic acid, benzaldehyde, carbon disulphide, glycerol, ethylene glycol, ethyl acetate, methyl acetate, furfural
Sulphuric acid	Chlorates, perchlorates, permanganates

Source: National Research Council – Prudent Practices in the Laboratory