

Chemical safety training

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Overview of chemical hazards

Health hazards

- ▶ **chemical burns**: skin corrosion and eye damage
 - ▶ **toxicity**: inhalation, ingestion (“eating”), skin contact
 - ▶ **long-term**: carcinogenicity, mutagenicity, reproductive toxicity
- ⇒ prevention and first-aid measures
- ▶ pregnant women must not work in the chemical laboratory!

Physical hazards

- ▶ **accidents**: fire and explosion; pressurized gas bottles, flammable stuff
- ▶ **leakage + corrosion** of metals, glass (HF), plastics (acids, solvents)
- ▶ **degradation**: heat/air/water/light-sensitivity (keep separately small needed amount), spontaneous oxidation ⇒ use inert gas, glove-box

Environment hazards and protection

- ▶ **limit** the reaction by-products, optimize isolation of final products
- ▶ **disposal** of dangerous waste: chlorinated hydrocarbons, heavy metals
- ▶ impact on aquatic life, ozone layer ((hydro)chlorofluorocarbons – HCFC, CFC – freons), greenhouse effect (SF₆, CF₄, N₂O)

Laws, regulations and labeling

Slovak legislation

- ▶ laws: 67/2010 (chemical law), 355/2007 (public health) – medical checks
- ▶ regulations: 355/2006 (chemical protection), 356/2006 (carc., mutagens)

EU: Regulations (EC) of the European Parliament and of the Council

- ▶ 1907/2006 (REACH) – registration, evaluation (producers, distributors)
- ▶ 1272/2008 – classification, labeling, packaging (adopts GHS norms of UN)



explosive flammable oxidizing press.gas corrosive toxic irritating harmful aquat.hazard

- ▶ package label: **name**, formula, **amount**, CAS number, EC number
- ▶ signal word: DANGER (higher risk), WARNING (lower risk)
- ▶ **H statements**: dangerous properties; P statements: precautions, storage
- ▶ MSDS: Material Safety Data Sheet – available for each substance

Operating regulations & procedures, risk assessment, proper ventilation, waste disposal

Labeling: H and P statements

H statements: standardized hazard sentences with assigned number

- ▶ HF(aq): **H300+H310+H330** Fatal if swallowed, in contact with skin or if inhaled.
- ▶ toluene: H statements and corresponding *Hazard category codes*
H225 Highly flammable liquid and vapour. (*Flam.Liq.2*)
H304 May be fatal if swallowed and enters airways. (*Asp.Tox.1*)
H336 May cause drowsiness or dizziness. (*STOT SE 3*)
H361d Suspected of damaging the unborn child. (*Repr.2*)
- ▶ acetone: **EUH 066** Repeated exposure may cause skin dryness or cracking.

P statements: precautionary statements

- ▶ *general*: **P103** Read label before use.
- ▶ *prevention*:
P210 Keep away from heat/sparks/open flames/hot surfaces. — No smoking.
P280 Wear protective gloves/protective clothing/eye protection/face protection.
- ▶ *response*:
P301+P330+P331 IF SWALLOWED: rinse mouth. Do NOT induce vomiting.
- ▶ *storage*: **P403+P233** Store in a well-ventilated place.Keep container tightly closed.
- ▶ *disposal*: **P501** Dispose of contents/container to ...

Hazard labeling + examples

Old (one-letter) vs. new abbreviations (lower number = higher danger)

- ▶ extremely flammable (**F+**) – *Flam.Liq./Sol./Gas 1* (ether, H₂)
- ▶ highly flammable (**F**) – *Flam.Liq./Sol./Gas 2* (acetone)
- ▶ oxidizing (**O**) – *Ox.Liq./Sol.1* (HClO₄), *2* (H₂O₂, KMnO₄), *3* (HNO₃)
- ▶ corrosive (**C**) – *Skin Corr.1A* (NaOH, HNO₃), *1B* (HCl), *1C* (KMnO₄); *Eye Dam.1* (cyclohexanone, H₂O₂); metals: *Met.Corr.1* (H⁺, OH⁻, Ga)
- ▶ very toxic (**T+**) – *Acute Tox.1* (HF), *2* (Be, Cd, Hg, CrO₃)
- ▶ toxic (**T**) – *Acute Tox.3* (CH₃OH); also following (only category 1):
- ▶ Carcinogenicity, Reproductive toxicity, Germ cell mutagenicity
Carc./Repr./Muta. 1A proven human, *1B* animals, *2* suspect
⇒ examples: *Carc.1A* (H350: CrO₃ or H350i-inhalation: NiSO₄),
Repr.1A (H360D-child: Pb), *Repr.1B* (H360D-child: Hg, NMP, DMF, DMA, NiSO₄, or H360F-fertility: CoCl₂, or H360FD-both: H₃BO₃),
Muta.1B (CrO₃, CdSO₄)
- ▶ specific target organ toxicity by repeated exposure (*STOT RE 1*): Hg, Be (blood), Cd (bones, kidney), Ni (lungs), CHCl₃ (liver, kidney)
- ▶ spec. target organ tox. single exposure (*STOT SE 1*): CH₃OH (eyes)


Ordering and storage directions (T, T+)



Very toxic (T+)

- ▶ *Acute Tox.1* or *2*: H300 (oral), H310 (skin), H330 (inhalation)
- ▶ forbidden to sell to individuals; can be ordered only with **my approval**
- ▶ provide me a copy of delivery note, and put “**chemikálie (T+)**” into accounting record
- ▶ must be stored in a locked metal box + Book of toxic substances
- ▶ every usage must be signed by the responsible person of the laboratory (Šiffalovič, Sabo)

Toxic, carcinogenic, mutagenic (T)

- ▶ *Acute Tox.3*: H301 (oral), H311 (skin), H331 (inhalation)
 - ▶ spec. target organ tox. single exposure (*STOT SE 1*): H370,
repeated exposure (*STOT RE 1*): H372
 - ▶ *Carc.1A* or *1B*: H350, *Muta.1A* or *1B*: H340
- }  (long-term tox.)
- ▶ provide me a copy of delivery note, and put “**chemikálie (T)**” into accounting record
 - ▶ Book of toxic substances: inventory record (who takes care of given bottle + amount)

Overview of the frequently used acronyms

GHS – Global Harmonised System of classification and labeling (by UN)

CAS – Chemical Abstract Service – unique number for each substance

NPEL – highest permissible exposure limit (Slovak law 355/2006) – allowed long-term concentration in the air, with no detrimental effects

OEL – Occupational exposure limit – (minimum) values prescribed by EU: either mandatory or indicative (“qualified estimate”)

BLV (slk. BMH) – Biological limit value – maximum concentration in a biological sample: urine, blood, air from alveols

TSH – Limit values (slk. Technická smerná hodnota: law 356/2006) – for carcinogens and mutagens: minimum measurable/achievable average concentration in the workplace (still, a no-threshold action is assumed)

PCB, PBB – polychlorinated biphenyls, polybrominated biphenyls

PBT – persistent, bioaccumulative and toxic substances

vPvB – very persistent and very bioaccumulative substances

CMR – carcinogens, mutagens or substances with reproductive toxicity

SVHC – Substances of Very High Concern – a list published by European Chemical Agency (ECHA), requiring special authorization for use

ADR/RID – international treaties about road (ADR) and railway (RID) transport of chemicals and gases – they affect producers and distributors

Information on our web-site (intranet)

STRÁNKA SAV KONTAKTY INTRANET FÚ WEBMAIL Hľadaj... EN

1 heslo: fyziksav

4 English

SAV FYZIKÁLNY ÚSTAV SAV, v. v. i.

O NÁS VEDA A VÝSKUM VZDELÁVANIE DOKUMENTY VEREJNOSŤ LINKY

CHRÁNENÉ HESLOM: INTRANET FÚ

Akreditačné podklady

BOZP ▾ 2

Základné pojmy

Civilná ochrana

» Chemická bezpečnosť

Požiarna ochrana 3

Školenia

Dokumenty THS

Pošli webový formulár ▶

Ústavné dokumenty

Zasadačka 295

Ochrana osobných údajov

Etická linka

Chránené heslom: Chemická bezpečnosť

MSDS

Kontaktná osoba pre FÚ SAV, v. v. i.: Anton Repko, miestnosť 191 v budove ChÚ, tel. 02/59410 536.

- Zoznam a vlastností chemikálií používaných vo FÚ SAV 2021 / verzia pre tlač, iba zoznam
- Starý systém upozornení podľa smerníc Rady 67/548/EHS a Komisie 2001/59/EC: R-vety (rizikové vlastnosti), S-vety (preventívne opatrenia).
- Nový systém GHS podľa OSN a nariadenia Európskeho parlamentu a rady (ES) č. 1272/2008: H vety (výstražné upozornenia), P vety (bezpečnostné upozornenia)
- Prevádzkový poriadok pre prácu s nebezpečnými chemickými faktormi (predbežná verzia) / PDF
- Klasifikácia nebezpečných vlastností podľa EÚ + GHS symboly / PDF
- Školenie chemickej bezpečnosti / PDF
- Chemická odolnosť rukavíc (latex, nitril, vinyl) / PDF
- Chemická odolnosť plastov / PDF

Safety measures and precautions: skin/eye burns

Lab. coat, goggles, gloves (disposable or lined), face shield, solid shoes



Especially dangerous chemicals (need more than just personal protection)

- ▶ HF(aq) (no glass/silicates!), conc. H_2SO_4 , HNO_3 , hot NaOH (aq)
- ▶ volatile compounds (HCl , NO_x , H_2S , NaOH aerosol): fume hood
- ▶ identify nearest wash basin, wiping tissues, shower, neutralizing ☉

Safety measures and precautions: other

Work with heat + some excluded conditions:

- ▶ flammable and volatile liquids: fume hood – no open flame
- ▶ open flame – remove all flammable stuff, identify nearest suitable fire extinguisher, use thick gloves or forceps/tongs etc.
- ▶ hydrocarbon solvents, reactive metals – don't extinguish with water
- ▶ reactions at elevated temperature: have at hand a cloth rag or something to hold hot vessels (to be able to remove violent reaction from the heating etc.); use reflux condenser (limit flammable vapors)

Electric cables and sockets: keep away from heat, water; easy to turn off

Storage of flammable and toxic compounds

- ▶ well closed and labeled vessels, firm placement, ventilation
- ▶ store **separately**: **oxidizing**, **flammable** and **toxic** stuff – risk of fire, but also toxic vapors, e.g. NO_2 from HNO_3 + alcohols, aromatic (benzene-like) compounds, metals (except Al/Fe/Cr: passivation)
- ▶ very toxic compounds have to be locked in a separate metal cabinet, responsible person, inventory record, use only with signed approval
- ▶ decontamination materials for the case of accident, solvent spill

Resistance of gloves and packaging materials

Gloves: for acetone/DMF use latex (white), for nonpolar use nitril (blue)

polyethylene (PE, LDPE, HDPE) and polypropylene (PP)

- ▶ suitable for polar solvents (water, alcohols, acetone (best: PP))
- ▶ not suitable mainly for chlorinated hydrocarbons and ethers

polyamide (PA), polyesters, polyethylene terephthalate (PET)

- ▶ suitable for hydrocarbons (petrol, hexane, toluene)
- ▶ not suitable for acids, hydroxides (beware of red polyamide spatulas)

polystyrene (PS) foamed or bulk (transparent), polycarbonate, polyacrylate (including instant glue), polymethylmetacrylate (PMMA)

- ▶ low resistance against org. solvents (rapidly damaged by acetone)
- ▶ foamed PS is suitable, e.g., for liquid N₂, dry ice with alcohol etc.

glass

- ▶ usually preferred over plastics + a cap/septum with PTFE layer
- ▶ not suitable for HF(aq) and F⁻; corroded also by molten NaOH

First aid

Chemical burns – skin, eye

- ▶ immediately rinse with water (and also think about suitable neutralization)
- ▶ remove contaminated cloths, continue with rinsing
- ▶ call medical help if necessary (155, 112); cooperation in work-place

Inhalation of irritating/suffocating gas/vapor (toxicity: LC50)

- ▶ move to fresh air, and ensure also the safety of others (fume hood, ventilation, neutralization)

Ingestion (swallowing) of toxic substance (LD50)

- ▶ check a suitable response in MSDS, section 4 (e.g., antidotes: Ca^{2+} for fluorides, thiosulfate for CN^- and heavy metals, active carbon)
- ▶ do not induce vomiting for: hydrocarbons (risk of lung damage), strong acids/bases (but drink plenty of water; perhaps add NaHCO_3)

Call local Poison center (Národné toxikologické informačné centrum, FNŠP Bratislava, Limbová 3, tel: +421(0)2 54774166)

- ▶ address and contact is given also in MSDS

Waste disposal

Liquid waste

- ▶ separate organic (oil), aqueous and solid phase (if possible)
- ▶ organic: separate disposal of non-halogenated and **halogenated** (chlorinated aromatic compounds have to be burned in a special way, to avoid the release of dioxins!)
- ▶ aqueous solutions: store phases with heavy metals (Pb, Cd, Hg, Ni)
- ▶ **Label** with approx. composition, keep well closed in a ventilated area
- ▶ some toxic substances can be safely neutralized (see webpage): F^- , CN^- , Ba^{2+} , Cr^{VI}

Solid waste

- ▶ cannot go into common waste if it contains highly toxic metals: Cd, Hg, As, Tl, Th, U (or a large amount of Ni, Pb, Se, Te, Be)

Empty bottles from volatile organic solvents

- ▶ **wash** with hexane/isopropanol/acetone and **dry well**
- ▶ remove label (using toluene) and dispose of with glass waste
- ▶ **danger**: ethers (e.g. diethylether, tetrahydrofuran, dioxane) form explosive peroxides on light and air (can be reduced with $HCl+Zn$)

Waste disposal

Reactive chemicals

- ▶ halogenides of Si, P: first wash and dilute by ethanol, then add water, NaOH/KOH
- ▶ Li/Na/K and corresponding organometalics: ethylacetate (or acetone), methanol, then dilute by water

Lead compounds

- ▶ PbI_2 – dissolves in $\geq 30\%$ HNO_3 , leaving solid iodine
- ▶ I recommend to have two washing baths in fume-hood: with 30% HNO_3 , and with water; nitrate solution can be the processed by electrolysis with Pt electrodes to gain PbO_2 (or Pb) – done by me
- ▶ don't add toluene nor DMSO (dimethyl sulfoxide)!
- ▶ insoluble $PbSO_4$: dissolve in $\geq 10\%$ NaOH, precipitate the carbonate by HCO_3^- , flush with water, then dissolve in HNO_3 (see above)

Mercury

- ▶ hand out to Safina company (free of charge)

Carbon nanotubes, graphene, freons

- ▶ incinerate at high temperature (contact me)

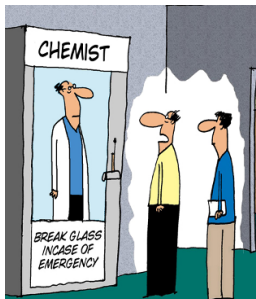
Environment protection

Before starting an experiment, **think about**:

- ▶ how to minimize consumption and leakage of dangerous materials (e.g. don't contaminate vessels from the outside)
- ▶ how the products will be stored + **proper labeling!**
- ▶ minimize waste and ensure its proper disposal
- ▶ how to clean the apparatus (to be able to use it again)
- ▶ manipulation with light-, air- and water-sensitive substances etc. (to minimize losses and failures)
- ▶ in the case of doubt, probe the properties and reactions with a small amount

Label your samples, use appropriate naming/numbering scheme, write all details in your **laboratory logbook**

Work safely!



Contact me if you have any questions (anton.repko@savba.sk, room 191)!