A SIMPLE MATRIX FOR TOXICOLOGICAL CATEGORIZATION OF MATERIALS WHERE R-PHRASES ARE NOT AVAILABLE IN THE CONTROL-BANDING PROCESS

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Topic Discussions

- Sources of Health Hazard Ratings (Limited Comparison)
  - EU Risk Phrases – the e-COSHH essential
  - HMIS vs. NFPA
    - Acute vs. Chronic Hazards / Risks
  - Converting Safety Data Sheet (SDS) Hazard Phrases to Risk Phrases
- Simple Matrix to Convert SDS Health Hazards to Risk
- Assigning Controls to manage risks
- Assigning PPE to manage risks

Control Bands Require Categorization of Hazards into Risks

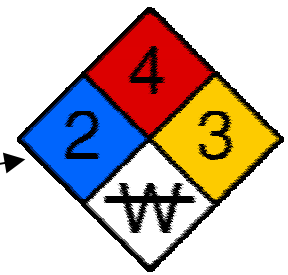
- Health Hazards
  - SDS
- Health Risks
  - EU Risk Phrases
  - NFPA
  - HMIS

Hazards → Qualitative Risk Assessment → Control Bands

Categorizing Health Hazards to Risks

- EU Risk Phrases
  - Categorizes chemicals that are “DANGEROUS”

☒ NFPA Standard 704 ….
  - Identification of Fire Hazards of Materials
  - Acute effects only



☒ HMIS®
  - HMIS® is not intended for emergency circumstances
  - Identifies risk category with ‘*’ for chronic effects

? SDS hazards → Risk?
  - Detailed compilation of hazards

Consider These Limitations

- R-Phrases –
  - Some countries do not have knowledge of R-phrases
  - Does not assign phrases to chemicals considered “not dangerous”
- NFPA designated for acute effects or “fire hazard” situations
  - Not specific .. can’t use the designation
  - Chronic hazards needed
  - Not readily accessible on SDS
- HMIS categories identify risks
  - Can’t use the designation #, & target organ effects may not be listed
  - Not on SDS
- SDSs
  - Expertise required to determine the “RISK”
  - Statements are far from standardized

Health Hazard Risks Considered for Control Banding

- [ ] R20
- [ ] R20/21
- [ ] R20/21/22
- [x] R20/22
- [ ] R21
- [ ] R21/22
- [ ] R22
- [ ] R23
- [ ] R23/24
- [ ] R23/24/25
- [ ] R23/25
- [ ] R24
- [ ] R24/25
- [ ] R25
- [ ] R26
- [ ] R26/27
- [ ] R26/27/28
- [ ] R26/28
- [ ] R27
- [ ] R27/28
- [ ] R28
- [ ] R34
- [ ] R35
- [ ] R36
- [ ] R36/37
- [ ] R36/37/38
- [ ] R36/38
- [ ] R37
- [x] R37/38
- [ ] R38
- [ ] R40 Carc cat 3
- [ ] R40 Muta cat 3
- [x] R41
- [ ] R42
- [x] R42/43
- [ ] R43
- [ ] R45
- [ ] R46
- [ ] R48/20
- [ ] R48/20/21
- [ ] R48/20/21/22
- [ ] R48/20/22
- [ ] R48/21
- [ ] R48/21/22
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- [ ] R48/23/25
- [ ] R48/24
- [ ] R48/24/25
- [ ] R48/25
- [ ] R49
- [ ] R60
- [ ] R61
- [ ] R62
- [ ] R63
- [ ] R64
- [ ] R65
- [ ] R66
- [ ] R67
- [ ] R68 Muta cat 3

- [ ] None of the above R-phrases apply.

If you wish to see a full description of what the R-phrases mean click here

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Some Countries Don't Use R-Phrases

- How can employers and workers convert hazard phrases from SDSs into "Risk Phrases"?

Difficult to Categorize Phrases

- Stated in scientific terms …. need experts to decipher
  - How do we qualitatively determine the risk from the hazard?
  - Are effects reversible?
  - Are effects lethal?
  - Sensitizers? Weak… moderate…. strong?
  - Skin notations?
  - Carcinogenicity notations?

International Mandate

- An international mandate to harmonize was adopted at the United Nations Conference on the Environment and Development (UNCED) in 1992 in Brazil:

  - *A globally-harmonized hazard classification and compatible labeling system, including material safety data sheets and easily understandable symbols, should be available, if feasible, by the year 2000.*

What should be done until this effort is reality?

Need a simplified matrix!

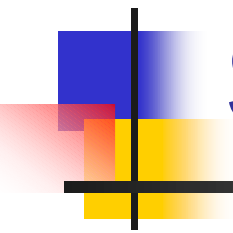
Health Hazards to Consider:

- Acute Toxicity
- Skin Corrosion/Irritation
- Serious Eye Damage/Eye Irritation
- Respiratory or Skin Sensitization
- Germ Cell Mutagenicity
- Carcinogenicity
- Reproductive & Developmental Toxicity
- Target Organ Systemic Toxicity – Single & Repeated Dose

Can We Categorize SDS Phrases?

Options:

- Use EU Risk Phrase categories
  - Difficult to “back track” without an expert
- Use regulatory definitions of hazard categories
  - Expertise required
- Use NFPA acute effect categories
  - Only for acute health hazards.. would work to match the category definition
- Use HMIS® III categories
  - Match the category number and ‘*****’ to category



Simplified Matrix

SDS Phrases vs. R-Phrases

Until a global harmonized R-Phrase system is available, could categorize SDS statements according to:

- **Not Dangerous / Hazardous**
- **Harmful: Caution**
- **Toxic: Warning**
- **Very Toxic: Dangerous**

R-Phrases	Statement
R20	Harmful by inhalation
R20/21	Harmful by inhalation and in contact with skin
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed
R20/22	Harmful by inhalation and if swallowed
R21	Harmful in contact with skin
R21/22	Harmful in contact with skin and if swallowed
R22	Harmful if swallowed
R36	Irritating to eyes
R36/37	Irritating to eyes and respiratory system
R36/37/38	Irritating to eyes, respiratory system and skin
R36/38	Irritating to eyes and skin
R37	Irritating to respiratory system
R37/38	Irritating to respiratory system and skin
R38	Irritating to skin
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
R68/20	Harmful: possible risk of irreversible effects through inhalation
R68/20/21	Harmful: possible risk of irreversible effects through inhalation and in contact with skin
R68/20/21/22	Harmful: possible risk of irreversible effects through inhalation, in contact with skin and if swallowed
R68/20/22	Harmful: possible risk of irreversible effects through inhalation and if swallowed
R68/21	Harmful: possible risk of irreversible effects in contact with skin
R68/21/22	Harmful: possible risk of irreversible effects in contact with skin and if swallowed
R68/22	Harmful: possible risk of irreversible effects if swallowed

Toxic: Warning

R-Phrases	Statement
R23	Toxic by inhalation
R23/24	Toxic by inhalation and in contact with skin
R23/24/25	Toxic by inhalation, in contact with skin and if swallowed
R23/25	Toxic by inhalation and if swallowed
R24	Toxic in contact with skin
R24/25	Toxic in contact with skin and if swallowed
R25	Toxic if swallowed
R33	Danger of cumulative effects
R34	Causes burns
R40	Limited evidence of a carcinogenic effect
R41	Risk of serious damage to eyes
R42	May cause sensitization by inhalation
R43	May cause sensitization by skin contact
R42/43	May cause sensitization by inhalation and skin contact
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

Very Toxic: Dangerous Including Long-Term Effects

R-Phrases	Statement
R26	Very toxic by inhalation
R26/27	Very toxic by inhalation and in contact with skin
R26/27/28	Very toxic by inhalation, in contact with skin and if swallowed
R26/28	Very toxic by inhalation and if swallowed
R27	Very toxic in contact with skin
R27/28	Very toxic in contact with skin and if swallowed
R28	Very toxic if swallowed
R30	Can become highly flammable in use
R32	Contact with acids liberates very toxic gas
R35	Causes severe burns
R39/23	Toxic: danger of very serious irreversible effects through inhalation
R39/23/24	Toxic: danger of very serious irreversible effects through inhalation and in contact with skin
R39/23/24/25	Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed
R39/23/25	Toxic: danger of very serious irreversible effects through inhalation and if swallowed
R39/24	Toxic: danger of very serious irreversible effects in contact with skin
R39/24/25	Toxic: danger of very serious irreversible effects in contact with skin and if swallowed
R39/25	Toxic: danger of very serious irreversible effects if swallowed
R39/26	Very Toxic: danger of very serious irreversible effects through inhalation
R39/26/27	Very Toxic: danger of very serious irreversible effects through inhalation and in contact with skin
R39/26/27/28	Very Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed
R39/26/28	Very Toxic: danger of very serious irreversible effects through inhalation and if swallowed
R39/27	Very Toxic: danger of very serious irreversible effects in contact with skin
R39/27/28	Very Toxic: danger of very serious irreversible effects in contact with skin and if swallowed
R39/28	Very Toxic: danger of very serious irreversible effects if swallowed

Very Toxic: Dangerous Including Long-Term Effects

R45	May cause cancer
R46	May cause heritable genetic damage
R48	Danger of serious damage to health by prolonged exposure
R48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation
R48/20/21	Harmful: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin
R48/20/21/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R48/21	Harmful: danger of serious damage to health by prolonged exposure in contact with skin
R48/21/22	Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed
R48/22	Harmful: danger of serious damage to health by prolonged exposure if swallowed
R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation
R48/23/24	Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin
R48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R48/23/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R48/24	Toxic: danger of serious damage to health by prolonged exposure in contact with skin
R48/24/25	Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed
R48/25	Toxic: danger of serious damage to health by prolonged exposure if swallowed
R49	May cause cancer by inhalation

Building the Matrix: Negligible Effects

Acute Effects				Exposure Limit		
Oral **LD50- Rats** **(Mg/Kg)**	**4 Hr.** **Inhalation LC50- Rats (Vapor)** **(Mg/m3)**	**4 Hr.** **Inhalation LC50- Rats (Aerosol)** **(Mg/m3)**	**Skin** **LD50- Rabbits** **(Mg/Kg)**	**OEL** **PPM (vapor)**	**OEL** **(mg/m3) (dust)**	
				500-999	(5-10)	***NEGLIGIBLE Effect*** no danger classification present no symbol or R phrases assigned

Building the Matrix: Low Effects

Acute Effects				Exposure Limit		
Oral LD50- Rats (Mg/Kg)	**4 Hr. Inhalation LC50- Rats (Vapor) (Mg/m3)**	**4 Hr. Inhalation LC50- Rats (Aerosol) (Mg/m3)**	**Skin LD50- Rabbits (Mg/Kg)**	**OEL PPM (vapor)**	**OEL (mg/m3) (dust)**	
>2000	>20,000	>5000	>2000	50-499	(1-4.9)	***LOW Effect*** Symbols Xi: irritating (except sensitizing agent) R phrases R36 irritating to eyes R37 irritating to the respiratory system R38 irritation to skin

Building the Matrix: Moderate Effects

Acute Effects				Exposure Limit		
Oral LD50- Rats (Mg/Kg)	**4 Hr. Inhalation LC50- Rats (Vapor) (Mg/m3)**	**4 Hr. Inhalation LC50- Rats (Aerosol) (Mg/m3)**	**Skin LD50- Rabbits (Mg/Kg)**	**OEL PPM (vapor)**	**OEL (mg/m3) (dust)**	
200 - 2000	2000 - 20,000	1000 - 5000	400 - 2000	10 - 49	(0.1-0.9)	***MODERATE Effect*** Symbols Xn: harmful C: Corrosive R phrases R20 harmful by inhalation R21 harmful in contact with skin R22 harmful if swallowed R33 danger of cumulative effects R34 causes burns R40 possible risks of irreversible effect R41 risk of serious damage to eyes R42 may cause sensitization by inhalation (Xi) R43 may cause sensitization by skin contact (Xi) R62 possible risk of impaired fertility R63 possible risk of harm to the unborn child R64 may cause harm to breast fed babies

Building the Matrix: Serious Effects

Oral LD50- Rats (Mg/Kg)	4 Hr. Inhalation LC50- Rats (Vapor) (Mg/m3)	4 Hr. Inhalation LC50- Rats (Aerosol) (Mg/m3)	Skin LD50- Rabbits (Mg/Kg)	OEL PPM (vapor)	OEL (mg/m3) (dust)	
<200	<2000	<1000	< 400	<10	(<0.1)	***SERIOUS Effect*** Symbols: T : toxic T+:very toxic R phrases: **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** **R35 causes serious burns** **R39 danger of very serious irreversible effects** **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** **R60 may impair fertility** **R61 may cause harm to the unborn child**

Hazard	EU Risk Phrase	SDS Tox Description	PPE Assignment Prior to Risk Assessment
High / Danger	**4; T; T+**		
Carcinogenicity	**R45 may cause cancer**		Protect appropriate route of exposure with respirator or other PPE and engineering controls
Mutagenicity	**R46 may cause heritable genetic damage**		
Subchronic & Chronic	**R48 danger of serious damage to health by prolonged exposure**		
Carcinogenicity	**R49 may cause cancer by inhalation**		
Reproductive	**R60 may impair fertility**		
Developmental	**R61 may cause harm to the unborn child**		
Eye	**R35 causes serious burns; R39 danger of very serious irreversible effects**	Corrosive; Impairment of vision; blindness; · Splash Potential · Particles that could get under glasses · Working in areas with overhead splash potential	Chemical Goggles - no option
Skin Contact	**R24 toxic in contact with skin; R27 very toxic in contact with skin; R35 causes serious burns**	Short, single exposure may cause severe burns; prolonged repeated exposure may cause severe burns	Face shield; Protective gloves; Full skin coverage with appropriate barrier material
Inhalation	**R23 toxic by inhalation; R26 very toxic by inhalation;**	Excessive concentrations readily attainable & may cause death; single brief exposure may cause death (LC50 1-hr < 200 ppm or < 2 mg/liter	Appropriate respirator mandatory unless complete containment is verified for all aspects of the operation.. With no chance of release or emission
Skin Absorption	**R39 danger of very serious irreversible effects**	May be fatal if absorbed through the skin; LD50 < 200 mg/kg	All skin and mucous membranes protected with appropriate barrier PPE including but not limited to goggles, full hooded impervious suit, face shield; shoe coverings; etc.
Ingestion	**R25 toxic if swallowed; R28 very toxic if swallowed**	LC50 < 50 mg/kg; Single dose oral toxicity high or very high, severe burns of the mouth	Policy enforced for personal hygiene and no eating, smoking etc. plus decontamination of PPE prior to removal.

Hazard	EU Risk Phrase	SDS Tox Description	PPE Assignment Prior to Risk Assessment
Moderate/ Warning	**3; Xn: harmful; C: Corrosive**		
Long-Term Effects (Subchronic & Chronic)	R40 possible risks of irreversible effect		Protect appropriate route of exposure with respirator or other PPE and engineering controls
Reproductive	R62 possible risk of impaired fertility		
Developmental	R63 possible risk of harm to the unborn child		
Subchronic & Chronic	R64 may cause harm to breast fed babies		
Eye	R39 danger of very serious irreversible effects; R41 risk of serious damage to eyes	Moderate or severe irritation; some irreversible damage possible	Chemical Goggles - no option
Skin Contact	R21 harmful in contact with skin; R-43; R34 causes burns	Severe irritation; prolonged or repeated exposure may cause skin burns; allergic skin reaction in humans	Protective gloves; Skin coverage with appropriate barrier material based on potential for contact with the chemical; optional Face shield
Inhalation	R20 harmful by inhalation; R-45 (Cancer); R42 may cause sensitization by inhalation (Xi)	Excessive concentrations readily attainable & may cause death; single brief exposure may cause death	Appropriate respirator mandatory unless complete containment is verified for all aspects of the operation. Risk assessment of practices and engineering controls required to remove the respirator requirement.
Skin Absorption	R33 danger of cumulative effects; R43 may cause sensitization by skin contact (Xi)	A single prolonged exposure may cause absorption in harmful amounts; repeated exposure could cause death	All skin and mucous membranes with potential for exposure protected with appropriate barrier PPE; Risk assessment required of practices & engineering controls to remove the minimum PPE requirement.
Ingestion	R22 harmful if swallowed	Single dose or toxicity LC50 > 50 mg/kg < 500 mg/kg	Policy enforced for personal hygiene and no eating, smoking etc. plus decontamination of PPE prior to removal.

Caution - Harmful

Hazard	EU Risk Phrase	SDS Tox Description	PPE Assignment Prior to Risk Assessment
Low / Caution	**2; Xi: irritating (except. sensitizing agent: => 3)**		
Eye	R36 irritating to eyes; R41 risk of serious damage to eyes	Corrosive; Impairment of vision; blindness; · Projectiles · General protection	Chemical Goggles - no option
Skin Contact	R38 irritation to skin	Short, single exposure may cause severe burns; prolonged repeated exposure ay cause severe burns	Face shield; Protective gloves; Full skin coverage with appropriate light-weight barrier material
Inhalation	R37 irritating to the respiratory system	Excessive concentrations readily attainable & may cause death; single brief exposure may cause death (LC50 1-hr < 200 ppm or < 2 mg/liter	Appropriate respirator mandatory unless complete containment is verified for all aspects of the operation.. With no chance of release or emission
Skin Absorption	R21-Harmful in contact with skin	May be fatal if absorbed through the skin; LD50 < 200 mg/kg	All skin and mucous membranes protected with appropriate light weight barrier PPE
Ingestion	R-22 Harmful if swallowed	LC50 < 50 mg/kg; Single dose oral toxicity high or very high, severe burns of the mouth	Policy enforced for personal hygiene and no eating, smoking etc. plus decontamination of PPE prior to removal.

Hazard	EU Risk Phrase	SDS Tox Description	PPE Assignment Prior to Risk Assessment
Negligible / Precautionary	**1**		
Eye	N/A	No corneal injury; slight transient irritation; essentially non-irritating	Safety Glasses
Skin Contact	N/A	Slight transient irritation; essentially non-irritating	Lab coat or uniform; Light barrier gloves
Inhalation	N/A	No adverse effects, not likely to be hazardous; dust may cause irritation; exposure to vapors unlikely	None
Skin Absorption	N/A	LD50 >2000 mg/kg	Lab coat or uniform; Light barrier gloves
Ingestion	N/A	LD50 >2000 mg/kg	Policy enforced for personal hygiene and no eating, smoking etc. plus decontamination of PPE prior to removal.

Non-hazardous.... determination must be archived!

Typical Classifications of Acute Physical & Toxicological Hazards* (SDS → Risk Categories)

Signal Words / Hazard	Danger (High)	Warning (Moderate)	Caution (Low)	Not Classified as Dangerous
Flammability	**Flashpoint < 20°F** Extremely flammable liquid and vapor	**20°F ≤ F.P. < 100°F** Flammable liquid and vapor. Flammable Solid.	**100°F ≤ F.P. < 200°F** Combustible liquid and vapor.	**Flashpoint ≥ 200°F**
Reactivity	**Ready detonation or explosive decomposition at normal temperature and pressure**	**Normally unstable. Detonation possible with strong initiation. Violent reaction with water.**	**Unstable at elevated temperatures and pressures. Reacts nonviolently with water.**	**Essentially nonreactive**
Skin Absorption	**LD_{50} ≤ 200mg/kg** May be fatal if absorbed through skin.	**200 < LD_{50} ≤ 1000 mg/kg** A single prolonged exposure may cause absorption in harm-ful amounts; repeated exposure could cause death	**1000 < LD_{50} ≤ 2000 mg/kg** Repeated exposure may result in absorption of harmful amounts even though LD_{50} may be unknown or is > 2000 mg/kg.	**LD_{50} > 2000 mg/kg**
Inhalation	**LC_{50} ≤ 200 ppm or ≤ 2mg/liter** for 1 hr. Excessive concentrations readily attainable and may cause death; single brief exposure may cause death	**200 < LC_{50} ≤ 2000 ppm, or 2 < LC_{50} ≤ 20 mg/liter** for 1 hr. Excessive concentrations readily attainable and may cause death; single brief exposure may cause death	**LC_{50} ≤2000 ppm, or > 20 mg/liter** for 1 hr. Could be hazardous on single exposure; simple asphyxia; may cause irritation to upper respiratory tract/lungs/eyes; prolonged excessive exposure may cause adverse effects.	**LC_{50} >2000 ppm, or > 20 mg/liter.** No adverse effects; not likely to be hazardous; dust may cause irritation; exposure to vapors unlikely.
Ingestion	**LC_{50} ≤ 50 mg/kg** Single dose oral toxicity high or very high; severe burns of mouth.	**50 <LD_{50} ≤ 500 mg/kg** Single dose oral toxicity moderate or moderate to high.	**500 <LD_{50} ≤ 2000 mg/kg** Single dose oral toxicity low or low to moderate.	**LD_{50} > 2000 mg/kg**
Eye/Skin Contact **Eye** **Skin**	**Impairment of vision; blindness; corrosive.** **Short, single exposure may cause severe burns; prolonged, repeated exposure may cause severe burns**	**Moderate or severe irritation, injury.** **Severe irritation; prolonged or repeated exposure may cause skin burns; allergic skin reaction in humans.**	**Slight irritation; slight corneal injury.** **Slight to moderate irritation, even a burn on single, prolonged, or repeated exposure; allergic skin reaction in susceptible individuals**	**No corneal injury; slight, transient irritation. Essentially nonirritating**

Control Bands: D C B A

Summary

- In order to assign control bands, hazards must be converted to “risk”
- Need to globally harmonize this process
- During the “gap period”, need a simplified matrix to apply control bands
  - Based on SDS phrases or tox endpoints

- Questions?