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DOHSBASE

Single risk measures for mixture vapour exposure

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Mixture vapour exposure

- Not included in:
  - "gevaarlijkestoffen.zelfinspectie.nl"
  - ARBO "kennisdossier gevaarlijke stoffen".
  - Chesar, Stoffenmanager, ECETOC-TRA (first tier modelling)
- Included in (this presentation):
  1. DOHSBase Risk Assessment Score (RAS)
  2. "SER www.veiligwerkenmetchemischestoffen.nl"
  3. REACH: Critical component/DPD+
  4. IH sum-score: Critical impact

Example mixture

Equimolar liquid mixture of Phenol, Butanol & Cumene

- critical impact: respiratory irritants (R37/Scoel, DOHSBase).
- Local short-term effect: compliance testing against OEL_{15min}
- vapour concentrations can be combined

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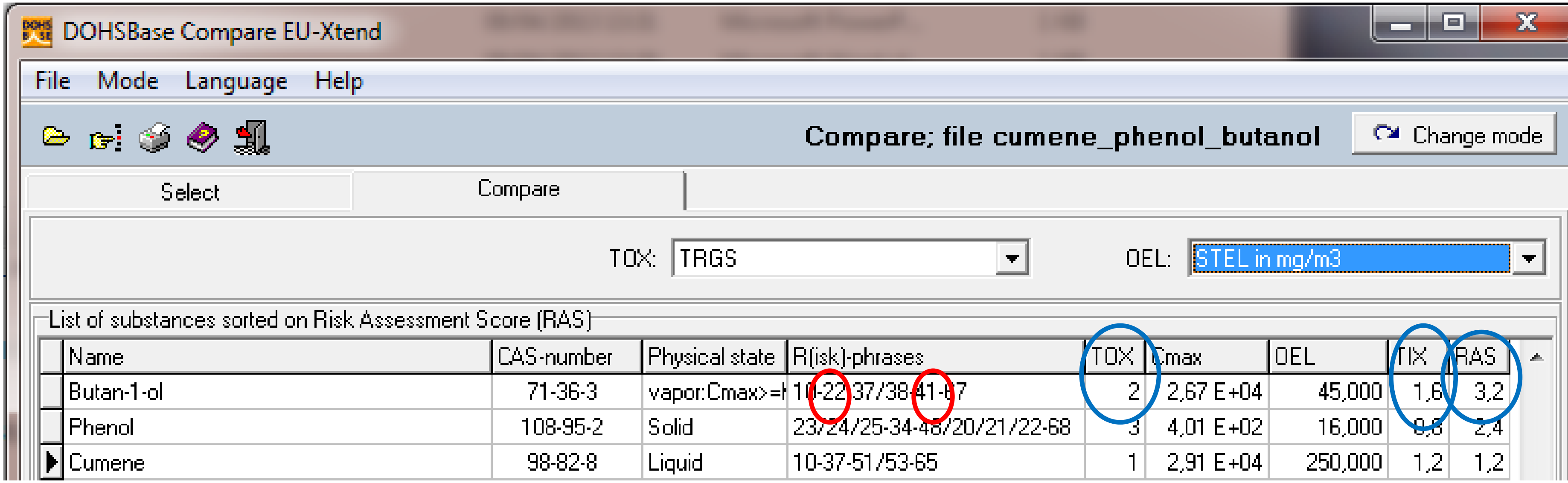
1. Risk Assessment Score



1. TOX = R-phrases -> TRGS-classes [1,2,3 or 4].
    1. nBut R22,41->TOX=2, Ph R68->Tox=3, Cumene R37,65->1
2. TIX = f(C_{max}/OEL) [range 0-4]
3. RAS = TIX*TOX [values between 0-16]

2. SER Guidance

Sign In

Veilig werken met chemische stoffen

Home

Search

Routes

- Veilige werkwijzen
- Veilige grenswaarden
- Werkplekfactoren

Achtergrond

- Veilige werkwijzen
- Veilige grenswaarden
- Werkplekfactoren
- Uw privacy

Begrippen

Contact

Portal

Route - Werkplekfactoren

Leidraad

$$\text{Som-score}: \sum_{i=1}^{i=n} \left(\frac{C_i}{OEL_i}\right) \leq 1$$

Inleiding

U bent bij het onderdeel werkplekfactoren aanbeland. Met dit deel van de route bepaalt u of het in uw situatie noodzakelijk is de grenswaarde te corrigeren. Deze aanpassing is noodzakelijk wanneer de manier waarop het werk wordt uitgevoerd, ervoor zorgt dat de gebruikte stoffen schadelijker of juist minder schadelijk voor de gezondheid zijn. Klik op deze link voor meer uitleg.

Het invullen van de vragen die horen bij de route werkplekfactoren duurt ongeveer 10 minuten. U krijgt achtereenvolgens vragen over:
* Uw achtergrond
* De duur van de blootstelling in de situatie die u wilt onderzoeken
* Eigenschappen van de stof(fen) waaraan medewerkers worden blootgesteld
* Eventuele huidopname
* Eventuele gelijktijdige blootstelling aan meerdere stoffen.

Indien blootstelling aan meerdere stoffen met hetzelfde optreedt, moet de gecombineerde blootstelling worden beoordeeld aan de hand van de som-score. Hierbij wordt de bepaalde concentratie van de stof, gedeeld door de bedrijfsgrenswaarde. Het resultaat van deze berekening wordt van alle stoffen met hetzelfde effect bij elkaar opgeteld. Indien het resultaat van deze optelling kleiner is dan 1, dan is de blootstelling afdoende beheerst.

In alle andere gevallen dient in het plan van aanpak te worden beschreven hoe de blootstelling verlaagd gaat worden en hoe tot dat deze verlaging is gerealiseerd, de medewerkers zullen worden beschermd. Beoordeel aan de hand van stofinformatie in hoeverre de stoffen daadwerkelijk hetzelfde effect of hetzelfde doelorgaan hebben.

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3. REACH: Critical component & DPD+

- Single mixture
- Per use (equal OC & RMM)
- Per exposure route
- grouped R-phrases

Exposure route	R-phrases	R-phrases
Inhalation	22, 25, 28	34, 35, 37
Oral	20, 23, 26	
Dermal	21, 24, 27	34, 35, 38
Eyes	34, 35, 36, 41	

3.1 Steps in DPD+ method (Cefic)

1. Classify mixture
   Stop if there are no human health R phrases
2. Select lead substance per exposure route (based on LSI)
3. Select ES and contributing scenarios of relevance based on routes for the lead substances
4. Extract OC and RMM
5. Combine and remove overlap, eliminate inconsistencies

3.1 DPD+, no OEL needed

- CMR / PBT/vPvB substances always LSI
- LSI_{inh} = partial vapour pressure / concentration limit for classification (C_{co})
- $LSI_{skin\ or\ oral}$ = Concentration in mixture / C_{co}
- Critical components → substance with highest LSI (and all substances with LSI >90% of this LSI)

3.1 DPD+ lead substance

- Calculate LSI_{inh}

Substance	Classification	Concentration in preparation (top of range)	Vapour pressure (Pa)	R-phrase(s)	class Conc'n limit	LSI
n-Butanol	10-22, 37/38, 41, 67	0.33	890	R37	0.2	1483.3
Phenol	23/24/25-34-48/20/21/22-68	0.33	10	R23	0.03	111.1
Cumene	10-22, 37/38, 41, 67	0.33	600	R37	0.2	1000.0

- N-Butanol = lead substance
- Combined exposure (R22, 25) → sum concentration
- OC & RMM for 100% n-Butanol

3.2 Critical component (Echa)

- DNEL needed for all substances in the mixture

1. Critical component selected based on highest RCR
   !!! Make OC & RMM equal   (Models may give different results)
2. Or potential for exposure → n-Butanol leading

Substance	Classification	Concentration in preparation (top of range)	Vapour pressure (Pa)	Mol wt	Limit value (mg/m3)	Maximum vapour concentration mg/m3	LSI
n-Butanol	10-22, 37/38, 41, 67	0.33	890	74.1	45	10135	225
Phenol	23/24/25-34-48/20/21/22-68	0.33	10	94.1	16	129	8.0
Cumene	10, 37. 51/53, 65	0.33	600	120.2	250	9864	39.5

4. IH sum-score

Three IH sum-score based methods to test compliance of vapours from a single liquid mixture with equal critical impact components:

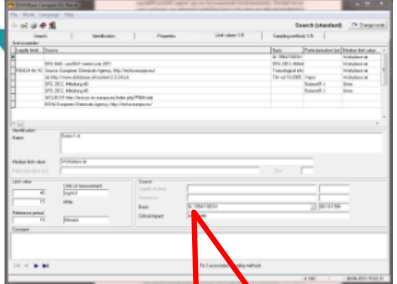
1. The ACGIH reciprocal method for hydrocarbons
2. The critical impact sum-score
3. The lead substance method (new?)

4.2 Critical impact sum-score

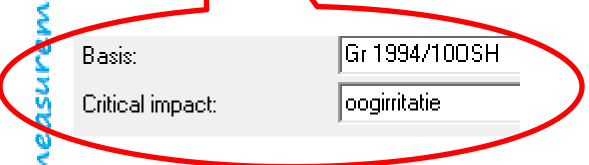
$$\sum_{i=1}^{i=n} \left(\frac{C_i}{OEL_i}\right) \leq 1$$

C_i the concentration in mg/m^3 of component i

components *i=1->n* with the same "critical impact"



4.2 Evaluation critical impact sum-score



- Its independent of the emission source.
- Requires to find equal critical impact (e.g. irritation or CNS) using R/H phrases or the critical impact mentioned by e.g. Health Council/TLV Doc
- Critical impacts are included DOHSBase OEL tab
- Requires to measure all relevant C_i in the mixture to test $\sum_{i=1}^{i=n} \left(\frac{C_i}{OEL_i}\right) \leq 1$

In a **single** mixture, C_i's are determined by their partial vapour pressures p_i **<u>which are mutual dependent</u>**.

So you can test one component with a p_i adjusted OEL

- 4.2a: Raoult ideal partial vapour pressures
- 4.2b: XLUnifac, correction for non ideal behaviour

The most comprehensive database of OEL's and measurement

4.3a Raoult's law

The vapour pressure of a single-phase mixture is *(in theory)* equal to the mole-fraction-weighted sum of the components' vapour pressures:

$$p_{tot}=\sum_{i=1}^{i=n} (p_i * X_i)$$

Where p_i is the mixture's vapour pressure, i is one of the components of the mixture and X_i is the mole fraction of the component in the liquid mixture.

$p_{i,x} = p_i * X_i$ is the partial pressure of component i in the mixture

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4.3a Raoult saturated sum-score(RIR)

$$\sum_{i=1}^{i=3}\left(\frac{c_{p\_x}}{16}+\frac{c_{b\_x}}{45}+\frac{c_{c\_x}}{250}\right)=26$$

components in the 1:1:1 M mixture	DOHBase vapor pressure p_i in Pa	Raoult (partial) $p_{i,x}$ in Pa	Raoult partial saturated $C_{i,x}$ in mg/m^3	Individual $OEL_{i,15min}$ in mg/m^3	Saturted OEL ratio (RIR-index) and sum-score	$OEL_{i,15m}$ in mg/m^3 in the vapor mixture
Cumene (c)	600.0	200.0	1001.7	250	4.0	38.52
n-Butanol (b)	890.0	296.7	916.2	45	20.4	35.24
Phenol (p)	20.0	6.7	26.1	16	1.6	1.01
Mixture		503.3	1944.0		26.0	

4.3a. Adjusted OELs in a liquid mixture to comply the sum-score

phenol, n-butanol, cumene

$$\sum_{i=1}^{i=3}\left(\frac{1}{16}+\frac{35.2}{45}+\frac{38.5}{250}\right)=1$$

Component OELs to keep the Sum-score<1

4.3a Evaluation lead substance using Raoult

- Critical impact compliance to the vapour of a single liquid mixture can be tested with a vapour pressure adjusted OEL of one component!
- Possible lead substance (=suitable DOHSBase measurement method):
  - Phenol: **No** -> BIA 8330/NIOSH 2546. LoD>10% OEL_{adj}=1 mg/m^3. Phenol in urine BLV_{adj} probably at or below background level
  - Cumene: **Yes**-> NVN 2949/2959, MDHS 80. **Diffusive** LoD<10% OEL_{adj} =38
  - Butanol : **Yes** -> NVN 2948/2987 , MDHS 72. Active LoD<10% OEL_{adj}=35
- However …. partial vapour pressures deviate from Raoult. They do not behave ideal according to $p_{i,x} = p_i * \boldsymbol{X_i}$

4.3b non-ideal liquid mixtures

For non-ideal cases: estimate (partial) vapour pressures using XLUNIFAC :

$$p_{a,tot} = \sum_{i=1}^{i=n} (a_i * p_{i,x})$$

Where a_i is the mixture's non-ideal vapour pressure activity coefficient and

$p_{a,x,i} = a_i * p_{i,x}$ is the adjusted partial vapour pressure of component i in the mixture.

4.3b component OELs in a non-ideal liquid mixture to comply the sum-score

phenol | n-butanol | cumene

$$\sum_{i=1}^{i=3}\left(\frac{.69}{16}+\frac{28.5}{45}+\frac{80.8}{250}\right)=1$$

		Raoult		XLUnifac non-ideal partial vapor pressure correction				
Compo-nents in the 1:1:1 M mixture	Individual $OEL_{i,15min}$ in mg/m^3	Partial vapor pressure $p_{i,x}$ in Pa	Adjusted $OEL_{i,15m}$ (mg/m^3) of the ideal vapor mixture	activity coefficient a_i	corrected vapor pressure $p_{a,i,x}$ in Pa	saturated $c_{a,i,x}$ in mg/m^3	Saturted OEL ratio (RIR-index) and sum-score	Corrected $OEL_{i,15min}$ (mg/m^3) of the vapor mixture
Cumene	250	200.0	**38.5**	1.95	390.8	1957.3	7.8	80.8
n-Butanol	45	296.7	35.2	0.75	223.9	691.4	15.4	**28.5**
Phenol	16	6.7	1.0	0.64	4.3	16.7	1.0	**0.7**
Mixture					618.9	2665.4	24.2	

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4.2b XLUnifac evaluation

- XLUnifac is used in process industry, but not validated in IH
- Recommended by Advanced Reach Tool

- Non-ideal behaviour of this mixture:
  - increases Cumene evaporation
  - decreases Phenol & Butanol evaporation
- Preferred lead substance (=precaution + measurement method):
  - Phenol: No -> LoD>10% $OEL_{adj,xlunifac}$
  - Cumene: Yes-> NVN 2949/2959, MDHS 80. **Diffusive** LoD<10% $OEL_{adj,raoult}$=38
  - Butanol : active LoD<10% $OEL_{adj,xlunifac}$=28, evaporation from mixture ↓

Proposed approach

1. Identify worst case with DOHSBase Compare RAS
   – Combine with use for non 1-mixture (next presentation, Rene Bekman)
2. With comparable RAS values and use, try SER sum-score
3. If SER sum-score is not feasible/realistic:
   – Single mixture, single source:
     - IH approach: Lead substance using Raoult (4.3a) or XLUnifact (4.3b -> ART, Stoffenmanager)
     - REACH : DPD+ (3.1) orcriticalsubstance (3.2)
   – Diffuse emission or several mixtures:
     - Reciprocal TLV method for hydrocarbons (4.1)
     - IH critical impact sum-score (4.2)
     - Sum-score with "effect specific limit values"

- Strategic and motivated choices
- So IH expertise stays required

Challenges

Include single mixture, single source method in DOHSBase ?

Integrate XLUnifac IH Sum-score approach in REACH CSR?

How to handle if precise information on (molar) concentrations in mixtures is not available?

(the real practice)

How to handle in REACH, exposure to several mixtures with (partly) the same components at one time ?

(the real practice)

NVvA 2014 !