



# ***Quantitative Assessment of Substance 'Unknown'***

*Exposure to ethane-1,2-dithiol*

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# What is the Problem?

- Concerns from operators after changing ethane-1,2-dithiol in Health Hazard Category communication system (HHC L.3 to L.1)
- Question from plants:
  - Is it true that when you smell ethane-1,2-dithiol that the concentration is above the OEL?

# Purpose of Research

- Assess operators' exposure during their work
- Assess exposure background
- Assess if odour threshold is below private OEL
- Check if concentrations are below private OEL

# Necessary Information

- Information ethane-1,2-dithiol
- OEL (Occupational Exposure Limit)
- Measurement Method
- Analytical Method

# Information Ethane-1,2-dithiol

- $C_2H_6S_2$
- Disgusting odour
- Odour threshold 0.12 mg/m<sup>3</sup> \*
- Vapor pressure 6.2 mbar at 20°C
- R-Phrases
  - R10: Flammable
  - R21: Harmful in contact with skin
  - R23: Toxic by inhalation
  - R25: Toxic if swallowed
- Ethane-1,2-dithiol is used in processes to make hormones like Desogestrel
- Ethane-1,2-dithiol is used to protect a functional place on the steroid molecule during chemical reactions

\* Handboek of Chemical Biological Warfare Agents, D. Hank Ellison, CRC Press

# Setting an Internal OEL for Ethane-1,2-dithiol

- NOEL Rat study 90 days 2,3-butaandithiol and 1,8-octaandithiol (WHO additives series 44): 0.70 mg/kg/day  
↓
- Extrapolation factor rat to human 10: 0.070 mg/kg/day  
↓
- Extrapolation factor subchronic to chronic 10: 0.0070 mg/kg/day  
↓
- Human 50 kg: 0.35 mg/day

OEL ethane-1,2-dithiol TWA 8 h:	0.035 mg/m <sup>3</sup>
OEL ethane-1,2-dithiol TWA 15 min:	1.12 mg/m <sup>3</sup>
Odour threshold (literature):	0.12 mg/m <sup>3</sup>

# Measurement Method

- Monitoring by KEMA Ned. B.V.
- Analytical method and analysis by DSM Research Geleen
- Monitoring based on analytical method
- Sampling Plan

# Analytical Method

- Literature study analysis methods
- NIOSH 2542 (analysis mercaptane) in combination with extraction and derivatisation of Dichloroethane extracts and GC-MS
- Determine detection limit of the analysis due to limits S-P
- Preparing and starting GC-MS with pure ethane-1,2-dithiol
- Choice and testing derivatisation method
- Analyse derivative di-TMS di-trimethylsilyl
- Calibration standards and optimizing GC method
- Assess recovery (> 99%)
- Assess conservation impregnated glassfiber filters (20 days)
- Compare wet method (impinger) with filter method

Active monitoring with constant flow air samplers in combination with impregnated glassfiber filter with mercury acetate, extraction, derivatisation and GC-MS detection (SIM detection and splitless injection)



# Results Measurements PAS CA1

Type of handling	Duration task (minutes)	Concentration during task (mg/m <sup>3</sup> )	Concentration during task if task duration is maximum in 8 hours (mg/m <sup>3</sup> )
Transfer ethane-1,2-dithiol from vessel to pressure vessel	19	<0.262	<0.010
Reactor A6 (stationary measurement)	287	<0.017	<0.010
Prepare centrifuge	52	<0.098	<0.011
Unload centrifuge in vessels by machine	2	<2.4	<0.010
Finish up centrifuge by hand	6	<0.833	<0.010
Scoop product on trays	22	<0.226	<0.010
Take sample from trays in tray dryer	0.4	<2.5	<0.010
Pour product on trays in drums	7.6	<0.132	<0.010

# Results Measurements PAS CA4

Type of handling	Duration task (minutes)	Concentration during task (mg/m <sup>3</sup> )	Concentration during task if task duration is maximum in 8 hours (mg/m <sup>3</sup> )
Put product from drum in reactor L (stationary measurement)	282	<0.008	<0.005
Tap water destillate layer	24	<0.11	<0.006
Break down water layer, open reactor, take sample	400	<0.006	<0.005
Unload scrubber	116	<0.02	<0.005

# Measurements Background

- All background measurements are below detection limit

## Extra Measurements

Type of handling	Duration (hours)	Concentration (mg/m <sup>3</sup> )
Long stationary measurement in dedicated room for transfer ethane-1,2-dithiol	24	<0.0016
Long stationary measurement at source	1.5	3.8

# Conclusions

- By one open handling per operator per day the private OEL TWA 8 h ( $0.035 \text{ mg/m}^3$ ) is not exceeded. Maximum concentration during one task is  $<0.011 \text{ mg/m}^3$ .
- By one open handling per operator per day the private OEL TWA 15 min. ( $1.12 \text{ mg/m}^3$ ) is not exceeded. For some of the measurements we can not draw a conclusion because of the short measurement time and the high detection limit.
- The 24 hour background measurement shows a concentration  $<0.0016 \text{ mg/m}^3$ .
- The odour threshold according to literature is not correct. It should be below  $0.0016 \text{ mg/m}^3$  instead of  $0.12 \text{ mg/m}^3$ .
- The air protection (fresh air hood) in combination with a Tyvek overall and gloves works well for exposure to ethane-1,2-dithiol (and APIs) and protects enough for the odour.

# Conclusion

Question:

- Is it true that when you smell ethane-1,2-dithiol that the concentration is above the OEL?

- Private OEL TWA 8 h 0.035 mg/m<sup>3</sup>
- Maximum concentration during one task is <0.011 mg/m<sup>3</sup>.
- Odour threshold <0.0016 mg/m<sup>3</sup> instead of 0.12 mg/m<sup>3</sup>

- The answer is NO