Chemical exposure of workers in cleaning stations for transport and storage tanks (containing chemical liquids): assessment and protection measures

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#### Summary:

Workers in tank cleaning stations are endangered by various hazardous substances in many cases of unknown chemical composition. Often used cleaning agents are xylene, acetone, methylethylketone (MEK), diesel fuel, sodium hydroxide, and phosphoric and hydrofluoric acid containing agents. Possible residue products to be eliminated are all chemical liquids with transport and cleaning allowance. The measurement results determined by thermodesorption must be regarded as background exposure. Multiple exceeding of limit values regarding to the values of e.g. benzene or triethylamine are a hint for possible maximum exposure of workers in tank cleaning stations and shows the necessity of good instructions to the workers and to make teaching of chemical basic knowledge standard practice.

#### Problem definition:

An increasing number of occupational diseases reported to us made it necessary to investigate the chemical exposure of workers in German tank cleaning stations. The objective was to obtain a valid number of base data to assess the individual exposure. Many cleaning agents and residue products in tanks are hazardous substances with limit values. High humidity (usually 100%) during the cleaning process and chemical aerosols contribute to the problem.

Sequences of a tank cleaning procedure with potential contact to hazardous substances:

- drive-in of the truck; possible contact to diesel fuel exhaust
- opening of the fill hole covers and visual control of the tank; possible contact to residue product

- manual application of cleaning agent when necessary, otherwise automatically; possible contact to cleaning agent
- lowering of the cleaning tool and starting of the automatic cleaning process (duration approximately 5 up to 60 minutes depending on the residue product); possible contact to cleaning agent and residue product
- manual flushing of tubes; possible contact to residue product and cleaning agents as aerosol
- opening of the drain valve (water, cleaning agent and residue product); possible contact to residue product and cleaning agent as aerosols
- manual inside cleaning and flushing of the tank when necessary; possible contact to cleaning agent and residue product
- tank drying with hot air



(fig.1: lowering of cleaning tools)

# Investigation:

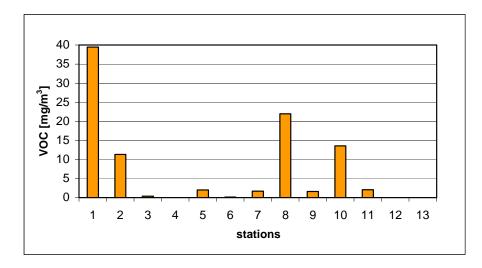
14 German tank cleaning stations were investigated using stationary and personal sampling methods. Analytical determination of air pollutants was made by established analytical methods by photo ionisation detector (PID) and by thermodesorption.

## Results and discussion:

14 Tank cleaning stations in total were investigated. They were selected having regard to number of cleaning tracks, year of construction and specialisation e.g. food tanks etc.. The objective was to have a good overview to exposure of workers in existing German tank cleaning stations. 13 tank cleaning stations were also investigated by thermodesorption. Thermodesorption is a proper method primarily to determine volatile organic compounds (VOC) at indoor work places. In two cleaning stations it was additionally possible to investigate the exposure of workers to single substances (benzene and triethylamine) One cleaning stations could not be investigated by thermodesorption due to pump failure.

#### Background exposure

VOC shown in figure 6 are workplace concentrations. In comparison, requirements for indoor concentration in Germany are exceeded multiple in some of the stations. The variation of the displayed results are best to be explained with the construction type of the stations. The concentration of hazardous substances in tank cleaning stations obviously depends on the construction type and the ventilation conditions. Open stations (outdoor-stations) have better ventilation conditions than closed stations with one or two gates. For this reason state of the art cleaning stations should be designed without gates if possible. Existing built-in stations should use exhaust devices on principle.

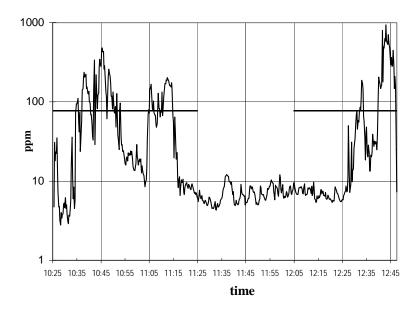


(fig. 6: VOC (average value measured by thermodesorption, measurement duration: 40 min. each))

Exposure to selected substances

1. Benzene

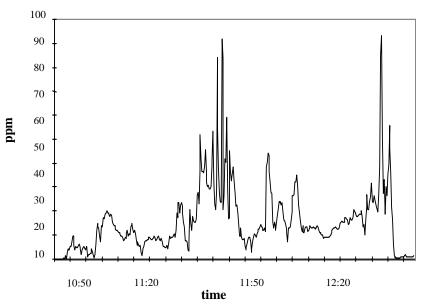
In one station the cleaning of benzene as residue product was accompanied by personal and stationary airsampling and gas-chromatography analysis. The measurement read-ups are shown in fig. 4 and fig. 5.



substance: benzene

average while sampling: 77,94 ppm

(fig. 2.: benzene exposure by time, hot cleaning)



(fig. 3.: benzene exposure by time, cold cleaning)

substance: benzene

average while sampling: 16,1 ppm Benzene concentration in fig. 2 and fig. 3 is shown in ppm (parts per million). Conversion in mg/m<sup>3</sup> can be done approximately as follows:  $C_{mg/m^3} = C_{ppm} \times 3.2$ . Used cleaning agents and scents are partly ionised because of the measurement principle. They are part of the measurement results (cross sensitivity).

residue product	average value	limit value	
	[mg/m <sup>3</sup> ]	[mg/m <sup>3</sup> ]	
benzene	65.9	3.2	

(fig. 4: stationary measurement, hot cleaning)

residue product	average value limit value	
	[mg/m <sup>3</sup> ]	[mg/m <sup>3</sup> ]
benzene	16.1	3.2
benzene	11.6	3.2
benzene	8.9	3.2
benzene	16.6	3.2

(fig. 5: stationary measurement, cold cleaning)

Results displayed in fig. 5 are measured after modification of the cleaning procedure from hot (fig. 4) to cold cleaning (fig. 5). The high effectiveness of reducing the cleaning temperature to minimise benzene disposal can be recognised. Additionally based on these results an exceeding of limit values could be assumed in case of substances with similar low limit values and similar volatility.

In comparison the average value of real-time PID-measurements (fig. 2 and fig. 3) shows good accordance to stationary ascertained values (see fig. 4 and 5). These results back up that real time gas monitoring by PID is suitable to show time dependent course of concentration although there is cross sensitivity to used cleaning agents, scents and humidity.

# 2. Triethylamine

Figure 7 shows results of a measurement during cleaning of a tank containing triethylamine as residue product. Due to disregard of prescribed cleaning methods by using a wrong cleaning agent (probably basic) a significant exceeding of the limit value occurred.

	residue product	average value	limit value
		[mg/m <sup>3</sup> ]	[mg/m <sup>3</sup> ]
stationary air sampling	triethylamine	54	4.2
personal air sampling	triethylamine	30	4.2

(fig. 7: measurement values for triethylamine)

The personal air sampling result is lower than the stationary because the worker did not stay at the container during the whole cleaning period. It is to be concluded from these results which demands are to be met to the person in charge, how necessary control and regard of prescribed cleaning methods are and of which importance a good instruction respectively basic chemical knowledge is.

During disregard of prescribed cleaning methods or bad ventilation conditions the permanent and safe compliance with limit values can not be guaranteed. Technical and organisational measures are necessary to reduce the chemical exposure in tank cleaning stations. As the result the following minimum requirements in tank cleaning stations should be met:

- use of database with information about adequate cleaning methods and safety information sheets
- use of personal protection equipment when necessary
- use of exhaust device on principle
- rejection of products with unknown ingredients
- preference of cold cleaning methods if possible
- preference of open designed cleaning stations
- instruction of workers in cleaning stations
- teaching of basic chemical knowledge

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