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INDUSTRIAL HYGIENE GUIDELINE:

The assessment of Exposure Vinyl chloride and 1,2-Dichloroethane

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SUMMARY

This document describes the assessment of the exposure to Vinyl chloride and 1,2 Dichloro ethane-dust in relation with the applicable occupational exposure limits. The guidance note is based on several documents from the European Centre of Normalisation (CEN), the Health and Safety Executive (HSE-UK) and the National Institute of Occupational Safety and Health-US (NIOSH) and has been reviewed by IndusTox Consult (Nijmegen Netherlands) who delivers services in the domain of exposure assessment of chemicals in the work environment. ■This guideline also incorporates the results of the validation studies that were performed to ensure that the methods are sensitive enough for the lower range of the recently applicable occupational exposure limits for Vinyl chloride and 1.2-Dichloroethane.

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1. INTRODUCTION

In the European Standard EN 689 “Guidance for the **Assessment of exposure by inhalation to chemical agents for comparison with limit values and measurement strategy**” a comprehensive exposure assessment approach is described with the aim to support among others:

- The characterization of the exposure to all potentially hazardous chemicals.....
- The prioritization of the assessment efforts.
- The judgment if the exposure profiles are acceptable.
- The identification of exposures that need additional information gathering

Monitoring data are mostly collected as additional information to help resolve, refine, or confirm the exposure profile.

The aim of this document “**Assessing of exposure to Vinyl chloride and 1,2-Dichloroethane**” is to give guidance on how to collect and judge these monitoring data and how to verify their representativity of the real exposure.

This guideline gives more specific information on how to perform compliance measurements in relation with the occupational exposure limit and how to define and to perform periodic monitoring that can be used for future epidemiological studies.

This standardized approach will also enhance the comparison of the results from all the sites.

This guideline is based on several documents from the European Commission of Normalization (CEN), HSE (UK) and National Institute of Occupational Safety and Health- NIOSH (USA) and has been reviewed by IndusTox Consult (Nijmegen Netherlands) who delivers services in the domain of exposure assessment of chemicals in the work environment. This guideline also incorporates the results of the validation studies that were performed to ensure that the methods are sensitive enough for the lower range of the recently applicable occupational exposure limits for Vinyl chloride and 1,2-Dichloroethane.

The decision logic used in this document to conclude on the acceptability of the exposure profiles is based on the internationally applied rule that for high hazard **chronic-acting substances**, the long-term average concentration over weeks or months is a better parameter than the calculation of the probability of exceeding the exposure limit. The Land’s “exact” procedure is a good statistical method to evaluate the mean concentration.

2. GENERAL PRACTICE

The common industrial hygiene practice is the following:

- 2.1. Exposure to Vinyl chloride and 1,2-Dichloroethane like for all chemicals should be kept as low as reasonably practicable.
- 2.2. In any case, exposure should not exceed the national legal occupational exposure limit.
- 2.3. Before every assessment, the validity of the exposure limits must be checked.
In table 1 a list of applicable exposure limits is given. (non exhaustive)

Table 1

Exposure Limit		TWA ¹		STEL		Adoption Date
		8 hour mg/m ³	ppm	15 minutes mg/m ³	ppm	
<u>Vinyl chloride</u>						
US ACGIH	TLV	2.6	1			2000
Europe	OEL	7.77	3			1999
<u>1,2-Dichloroethane</u>						
US / ACGIH	TLV	40	10			1996
US/ NIOSH	REL	4	1	8	2	2005
Austr ia	TRK	20	5	80	20	2007
Bulgaria	OEL	4	1	8	2	2004
Belgium	OEL	40	10			2009
Czech Republic	OEL	10	2.5			2007
Denmark	OEL	4	1			2008
Finland	OEL	4	1	20	5	2009
Hungary	OEL	10	2.5			2007
Ireland	OEL	20	5	40	10	2007
Italy	OEL	40	10			2008
Poland	OEL	50	12.5			2009
Netherlands	OEL	7	1.5			2008
Norway	OEL	4	1			2009
Portugal	OEL	40	10			2004
Romania	OEL	30	7	70	17	2006
Spain	OEL	20	5			2009
Sweden	OEL	4	1	20	5	2009
Switzerland	OEL	20	5			2009
UK	OEL	20	5			2007

1) Time-Weighted Average.

- **Unusual Work Schedules**

Normally the OELs are time weighted averaged for the conventional 8 hour day and the 40 hour week. In case the working shift is longer the OEL should normally be adjusted, but for Vinyl chloride and 1,2-Dichloroethane no correction factor is necessary.(by Law of Haber⁴).

- **Adequate control of exposure**

Where exposure to Vinyl chloride and Dichloro ethane cannot be avoided, control should be achieved by material, plant and process controls or other suitable control techniques. Only where those measures taken do not guarantee adequate control of exposure, suitable respiratory and other personal protective equipment should be worn.

3. **OBJECTIVES OF THE EXPOSURE ASSESSMENT**

Before the process starts, the exposure assessment goals must be clear to everyone involved in the assessment.

A strategy directed at assessing all exposure for all workers on all days is highly recommended. In addition to ensuring compliance with existing occupational limits (OELs), this strategy provides an understanding of the day-to-day distribution of exposures. Exposure assessment findings can then be used to address present-day health risks and to construct exposure histories. If a historical database is maintained, the exposure assessment data may be used to address future health issues for individual workers or groups of workers. In the latter case, the data may be used to support epidemiological studies.

The goals of a comprehensive exposure assessment include:

1. Characterization of the potential exposures to Vinyl chloride and 1,2-Dichloroethane ;
2. Characterization of the exposure intensity and temporal (hour-to-hour/day-to-day) variability faced by all workers;
3. Assessment of the potential risks (e.g.: risk of potential harm to employee health, risk of non-compliance with governmental regulations, etc...);
4. Prioritization and control of exposures presenting unacceptable risks;
5. Identification of exposures for which additional information is needed (e.g.: Initial monitoring, etc...);
6. Documentation of exposures and control of efforts, and communication of exposure assessment findings to all affected workers and to those who are involved in worker health protection (e.g.: management, occupational physician, engineering staff, etc...);
7. Maintenance of a historical record of exposures for all workers so that future health issues can be addressed and managed relative to actual exposure information;
8. Accomplishment of the preceding steps with an efficient and effective allocation of time and resources.

4. BASIC HARACTERIZATION

4.1 COMMON DESCRIPTION

The collection and organization of the available information on the workplace, the workforce, the agents, the historical exposure data, etc., to assess and evaluate health risks.

As a minimum, the following questions must be answered:

- What processes and operations, and what tasks and work practices, pose significant potential for worker exposures to Vinyl chloride and 1,2-Dichloroethane ?
- How is the work organized?
- What are the significant sources of exposure?
- What controls are in place, and how are they used?

4.2 WORKPLACE INFORMATION

Work involving Vinyl chloride and 1,2-Dichloroethane should be assessed in order to identify sources of exposure or the provision of new controls. The work should be re-assessed whenever changes are introduced which significantly affect the material, plant or process controls.

Preparing a written description and/or a schematic diagram of the process or operation can be used to identify sources of potential exposure, location of chemicals and tasks, ventilation and other control methods.

4.3 WORKFORCE INFORMATION

The goal of the work force characterization is to understand the division of labor and the work practices. Detailed knowledge of routine and non-routine work assignments, work schedules and tasks must be acquired. It helps to subdivide the workers in similar exposure groups, by describing jobs, tasks, and number of workers and frequency. The workforce characterization should be based on a variety of resources, including the plant's organigram, job descriptions, worker interviews, management interviews and most important, careful observation of work practices and the workplace. If in grouping workers, the industrial hygienist deviates from the personnel system, accurate records will be needed relating the similar exposure groups to the personnel record keeping system. Incongruence between industrial hygiene and personnel job classification schemes could make investigation of future issues difficult.

More and more, many workplaces rely on contract labor to perform routine and nonroutine work. It is important for contractors to be included in the exposure assessment process. The mechanism and requirements for assessing the exposure of contract labor should be

established in the contract. Larger or more sophisticated contractors may have their own exposure assessment capabilities. For other contractors, it might be more effective to rely on the skill and expertise of the client.

5. ESTABLISHING SIMILAR EXPOSURE GROUPS (SEG)

In most workplaces, it is difficult to measure personal exposures to all agents for every worker. Although there are examples of the daily use of dosimeters (e.g.: measuring ionizing radiation exposure), it is not practical and seldom possible. A strategy for meeting these challenges is to assemble workers believed to have similar exposures into a group.

Similar exposure groups (SEGs) are groups of workers having the same general exposure profile because of the similarity and frequency of the tasks they perform, the materials and processes with which they work, and the similarity of the way they perform the tasks. The qualitative or quantitative characterization of the exposure of one or a few workers in the group is then considered “representative” of the exposures of every worker in the group.

There are several strategies to establish the SEGs:

- Classifying by process, and agent;
- Classifying by process, job, and agent;
- Classifying by process, job, task, and agent;
- Classifying by process, task, and agent;
- Classifying work teams;
- Classifying non-repetitive work.

Similar exposures groups are established by observation using data gathered during characterization of the workplace, work force, and agents. SEGs established by observation are generally described by the following determinants: “process, job, task and agent”. This classification is the most often used, and also the method that is introduced in this document.

Classifying by Process, Task-Based and Agent Approach: Each job description is an entry represented by at least one worker on at least one day. Common examples are:

	%	tasks/nr	Duration (min)	HCl	Cl ₂	PVC	Noise
Operator VC							
Control Room	25	1	120				
Polymersation	25	2	60				
Dryers	10	2	24				
Filters	2	3	27				
Unblock	2	1	9				
Packer							
Filling bags	25	1	120				
Pelletize bags	25	2	60				
others	10	2	24				

6. AIR MONITORING

6.1 INTRODUCTION

A competent person in industrial hygiene shall define the air monitoring program. The goal of this program is to establish the sampling plan (e.g. sampling frequency, location, and sampling duration), selection of the air monitoring equipment, data evaluation and analysis of the samples and to verify:

1. whether the 8-hour time-weighted average concentrations of Vinyl chloride and 1,2-Dichloroethane in the breathing zone exceed the specified limits
2. if established control measures are functioning properly or if additional control measures are needed.

6.2 MONITORING OBJECTIVES.

There are different monitoring objectives or strategies that broadly can be grouped into three categories:

6.2.1 Initial Monitoring

In case the *basic survey* (e.g. EN689 / 5.1.4.2 or the company specific exposure assessment methodology) can not give sufficient information if an exposure profile of a Similar Exposure Group (SEG) is acceptable (< 10% of exposure limit) or unacceptable, (≥ 100% of exposure limit) the assessment of the exposure profile is uncertain.

In that case initial monitoring is mostly used to assess the compliance with an exposure limit. Only personal monitoring techniques are appropriate.

6.2.2 Periodic Monitoring

Periodic monitoring is used to evaluate periodically exposure profiles that are judged as acceptable and which have a mean concentration that is greater or equal to 1% and lesser than 100% of the exposure limit. (see 6.1.15)

If documented properly, periodic-monitoring data can also be used for future epidemiological studies.

In the case of periodic compliance monitoring, only personal monitoring techniques are appropriate

6.2.3 Diagnostic Monitoring

When trying to identify the exposure source and to understand how source, tasks, and other variables (e.g. production rates) contribute to worker exposure, diagnostic monitoring should be conducted. The results can help the industrial hygienist to define the most appropriate and efficient control strategies for unacceptable exposures.

If the source is from a fixed piece of equipment, area-monitoring techniques are appropriate. If the source moves with the worker or depends on individual work practices, personal monitoring techniques are appropriate. In most cases, measurement-averaging times should reflect process cycle times rather than the exposure limit averaging times. Using a longer averaging time will simply average out the actual data required for problem identification. For example when one intends to monitor the exposure during a task of 10 minutes but sampling time start 10 minutes before and continues 10 minutes after the task, you will measure a concentration $10^{2/30}$ of the real concentration during the task.

6.3 MONITORING METHODS

6.3.1 Personal air monitoring

The best estimate of an individual's exposure is obtained by taking breathing zone samples (personal sampling) for the entire working period. This optimum is not always practical and the actual sampling time should be arranged so that it covers certainly the potentially highest exposures, and at least 75% of the reference period.

Active sampling

The active sampling method is the most common method to assess the personal exposure to Vinyl chloride and 1,2-Dichloroethane of workers.

The principle is that a measured volume of air is drawn by a pump through an adsorption (activated coconut charcoal)-tube.

Passive or diffuse sampling

The theory of this sampling approach is that a sampler collects molecules transported to the adsorbent by molecular diffusion. The effective sampling rate of such a device can be predicted from Fick's law, provided that the diffusion constant of the compound is known. The passive monitors are critical to use in warm and humid climate conditions, as samples losses can become significant if the relative humidity exceeds 50 % and temperature is going up.

Diffuse sampler must be developed according the requirements of EN838. Without the use of correction factors, the monitors can be used between an air temperature range of 10 °C to 30 °C and a relative humidity range between 20 % and 80 %.

The circumstances during the measurements should be recorded: °C, humidity, and barometric pressure.

It should also be noticed that these diffusion monitors must have backup sorbent pads to detect breakthrough.

When a plant intends to use the passive sampling method, they should verify if manufacturers have performed adequate validation studies and they should prove the consistency between the passive and active method during field validations with simultaneous measurements. At present the active method is recommended as the reference sampling method, till there is *enough evidence to* prove the consistency of the passive method.

Attaching the sampling equipment on the worker

Attach the tube or (passive) monitor to the operator, in preference on the lapel, not more than 30 cm away from the nose-mouth region. The sorbent tube is connected to a pump that is attached to a belt around the waist of the worker. The tube should always be maintained in a vertical position so that there is no channeling in the activated charcoal

6.3.2 Area monitoring

Area (or fixed-point) measurements can be done with the same devices as used for personal air monitoring is used, but also with semi-continuous measurement devices (Gas Chromatography, Infrared, Mass Spectrometry). Area monitoring can be used to identify the background concentrations at the workplace and are useful to measure the effectiveness of control measures (e.g. local exhaust ventilation) over a period of time.

Area-point measurements should not be used to verify compliance with an exposure limit.

6.3.3 Direct Reading Monitors

A general feature of direct-reading instruments is the short average time, which makes these monitors suitable for objectives such as detection of peak exposures, emission source detection, and trend analyses of background concentrations.

If such a monitor has a datalogger, it can also be used to assess the compliance with the excursion limits or the STEL of a substance. One can monitor during the entire shift. This approach has the advantage that the whole shift is measured and that the mean concentration can be automatically calculated every 15 minutes of the shift. The "worst case" 15 minutes can be identified easily. All peak concentrations during the shift can also easily be identified.

At this moment these monitors have a too high detection limit in relation with the occupational limit value of Vinyl chloride of 1 ppm and therefore they are **not suitable** to assess the personal exposure of workers in comparison with the exposure limit. However, in many plants direct reading monitors are often used for a documented leak detection program (valves, pump gaskets, flanges, etc.)

A production site in France has tested the mini-RAE-PID and the TVA1000B-FID and they recommend the TVA1000B-FID because of its relatively low maintenance (every 3 months calibration instead of every week for the mini-RAE-PID). The TVA1000B-FID is also less sensitive for moisture.

It should be noted that portable FIDs or even PIDs have a detection level around 1 ppm (even if interference's are excluded), what means that these monitors can not be used for accurate personal exposure monitoring.

6.4 VALIDATED AND ANALYTICAL METHODS

Traditionally the analytical methods mostly used, are based on the NIOSH-1007 method or ISO 9762 method for Vinyl chloride and the NIOSH-1003 method for 1,2-Dichloroethane.

These classical methods and some other methods used in the field, using other adsorption material, diffuse sampling and thermal desorption, have not been validated in accordance with EN 482 and do not allow measurements below 10% of the lowest OEL's (see table 1):

- 1 ppm for Vinyl chloride (US/ TLV TWA 8 hours)
- 1 ppm for 1,2-Dichloroethane (Sweden/ OEL TWA 8 hours).

On request of the ECVM, the NMi from Delft in the Netherlands has performed validation studies ⁶⁾ for the methods most appropriate for the measurement of exposure to VCM and DCE in the here above mentioned concentration ranges.

6.4.1 Conclusions of the validation study

Classical methods

NIOSH-1007, ISO 8762 for Vinyl chloride and
NIOSH-1003 for 1,2-Dichloroethane

These methods are based on:

Pumped sampling on activated charcoal with carbon disulfide desorption

The criteria for 'overall uncertainty' were fulfilled under all conditions studied

Taking into account the following changes

- **Sample tubes containing 400+200 mg activated coconut charcoal**
- **Desorption with 3 ml CS₂**
- **For total sample volumes of 12 and 24 litres, 8 hours at a sampling, flow rate of 25 and 50 ml/minute**

For each of the conditions studied, the criteria given in EN 482 [1] for the ‘overall uncertainty’ (OU = bias + 2 times standard deviation \leq 50% for the level of 0,1 ppm or \leq 30% for the level of 2 ppm) are amply fulfilled, indicating the appropriateness for the purpose of the pumped sampling – solvent desorption method.

In Annex 4 you will find the full report⁶⁾ of the validation.

Other methods

Pumped sampling with thermal desorption

The methodology was found to give unsatisfactory results in all combinations with VCM and DCEa together.

Only for DCE without the presence of VCM, the sampling on Chromosorb 106 fulfilled always the criterion for ‘overall uncertainty’ as defined in EN 482.

DCE

- **Sample tubes containing 300 mg Chromosorb 106**
Sampled on Chromosorb 106 the ‘overall uncertainty’ always fulfilled the uncertainty criterion of EN 482.
 - For sample volumes of 9.6 litres, 8 hours 20 ml/minute

Diffusive sampling with thermal desorption

The methodology gives satisfactory results; the effective uptake rates determined for VCM on Unicarb and DCE on Chromosorb 106 fulfill the performance criteria of EN 482. For VCM sampled on Unicarb, the effects of increased temperature and relative humidity are significant, however, leading to an average effective uptake rate that nearly fulfills the ‘overall uncertainty’ criterion of EN 482.

VCM & DCE

- **Sample tubes: Perkin Elmer, type diffuse sampler with 300 mg Unicarb**
 - Conditions: 20°C and 30 °C, 50% and 88% relative humidity
 - Sample rate: VCM 1.25 ng/ppm.min, DCEa: 1.50 ng/ppm.min

DCE

- **Sample tubes: Perkin Elmer, type diffuse sampler with 300 mg Chromosorb 106**
- Conditions: 20°C and 30 °C, 50% and 88% relative humidity
- Sample rate: DCEa 2.01 ng/ppm.min

Diffusive sampling on activated charcoal badges

The results are acceptable for DCE when using both single-layer (3M 3500) and double-layer (3M 3520) badges. For VCM; when using the single-layer badge (3M 3500) the effective uptake rate varies largely with the concentration, the temperature and the relative humidity. Experiments with the 3M 3520 badge show a 40% decrease in effective uptake rate from 0,1 to 2 ppm concentration levels.

The use of these samplers for VCM is **not recommended**.

DCE

- 3M sampler 3500 and 3520
 - Conditions: 20°C and 30 °C, 50% and 88% relative humidity
 - Sample tubes: Perkin Elmer, type diffuse sampler with 300 mg Chromosorb 106
 - Sample rate: DCEa 29.1 mL/min/ (is recommended instead of 32.5 mL/min given by 3M).
 - Desorption with 1.5 ml CS₂.

In table 2 an overview is given of the conclusions of the validation results.

Table 2

<i>Desorption</i>	Pumped sampling				Diffusive sampling			
	CS₂		Thermal		CS₂		Thermal	
	VCM	DCE	VCM	DCE	VCM	DCE	VCM	DCE
Activated charcoal tube	Yes	Yes						
Chromosorb 106				Yes				Yes
Unicarb			No	No			Yes	Yes
Carbosieve III			No	No			No	No
Activated charcoal badge 3M 3500					No	Yes		
Activated charcoal badge 3M 3520					No	Yes		

Yes = method fulfills the performance criteria given in EN 482

In Annex 4 you will find the full report⁶⁾ of the validation.

6.4.2 Breakthrough during sampling

A standard charcoal tube (NIOSH methods) consists of 150 mg of activated charcoal, 100 mg in a front section and 50 mg in a back section. After the validation it is now recommended to use an activated charcoal of **600 mg**, 400 mg in a front section and 200 mg in a back section.

The two sections are separated in order to detect "breakthrough". The smaller section should always be downstream of the larger section. When a significant amount is found in the second section, breakthrough from the first section has occurred. In line with international recommendations (NIOSH, etc), if the second section holds less than 10 % of the mass of the first section ($W_B/W_F < 10\%$), one may conclude that no perceptible breakthrough occurred. Under this condition, the sample is valid and the sum of W_F and W_B is used to calculate the concentration.

This means that the laboratory must analyse the two sections separately and report the W_F and W_B to the industrial hygienist in charge of the measurement campaign.

Instead of using the two sections of the tube, also two tubes in tandem can be used. In this case the total charcoal amount of each tube must be analysed.

If the ambient temperature rises ($>22^\circ\text{C}$), the possibility of breakthrough should be considered when sampling by the NIOSH method. At ambient temperatures of 40°C a significant loss of more than 30% was observed. ⁽⁵⁾

6.4.3 Maximum flow rate and sample volume

It is very important that the industrial hygienist, when using a sorbent tube and in order to avoid unacceptable breakthrough, will not exceed the total volume of air that may be sampled for the specified method

NIOSH defines a breakthrough volume (V_b) in its analytical methods for relatively worst-case conditions. Breakthrough volume is the maximum volume that can be sampled, when relative humidity (RH) $\leq 80\%$ and the airborne concentration = 2 x the occupational exposure limit, so that $W_B/W_F < 10\%$.

If we want to modify the flow rate or the total amount of sorbent etc of the existing methods, additional validation is needed

6.4.4 Storage and transport

Use a freezer for storage and transport of the tubes or badges.

6.4.5 Attaching the sampling equipment on the worker

Attach the sampler head to the operator, in preference on the lapel, not more than 30 cm away from the nose-mouth region. The sampler head is connected to the pump that is attached to a belt around the waist of the worker.

The limit of detection (LOD) of material that can be weighed with a balance with a weighing precision of 10 µg, is approximately 300 µg. For example at an air concentration of 0.5 mg/m³ it is necessary to collect a volume of 0,6 m³ air to achieve this.

6.4.6 Quality control

Responsibility monitoring program.

The person who is responsible for the assessment should have enough experience and background to perform this assessment and monitoring program.

Analytical laboratory.

Before deciding which analytical laboratory is going to analyze the tubes or badges, calibrating the pumps, one should verify if this laboratory is certified to perform these activities.

- Is the laboratory certified by an external control agency: ISO, GLP, etc?
- Is the Laboratory Analyst qualified by training?
e.g. specific education, on the job, course, etc.
- Is the laboratory participating in Round Robin performance tests?
- Does the laboratory uses laboratory blanks to check the accuracy of the analytical method?
A **media** (laboratory) blank is an unexposed tube or badge, not taken to the **field** (e.g. plant), used for background correction of sample readings or for recovery studies.
- Do they have the coefficient of variation of their analyses?

If one or more of these questions is answered negative, one should consider to look for an other laboratory!

Sampling

In order to check the accuracy of the air sampling and analytical method one should :

- Submit routinely field blank samples to the laboratory along with field samples.
A **field blank** is a filter, handled exactly the same as the **field** samples, except no air is drawn through it.

6.5 AIR SAMPLING PLAN

6.5.1 General

To compare an exposure level of a substance with its exposure limit, one needs to know the concentration of the substance in the breathing zone extrapolated to the same reference period as that is used for the limit value (i.e. 8 hours for chlorides). At least 75% of the reference period should be sampled. However, if during more than 25% of the reference period no exposure occurs, a sampling time less than 75% is permissible. For work shifts greater than 8 hours, one should verify if the exposure limit must be adjusted and the sampling time should be 75% of the longer work shift .

Pump out or on when respirator is used?

In assessing the *compliance of a SEG* with the exposure limit, one should *sample the whole exposure period without taking into account the wearing of a respirator*. That is what you can interpret and read in European guidelines and OSHA standards:

"Employee exposure" and other similar language referring to the air agent level to which an employee is exposed, means the exposure to the airborne agent that would occur if the employee was not using respiratory protective equipment".

Only when workers are wearing respiratory protection offering a high level of protection with an assigned protection factor (APF) of 2000 (Self contained breathing apparatus full face mask positive demand (EN 137) or a compressed airline breathing apparatus positive demand full face mask (EN 139)), the sampling may be stopped during the time the person is wearing this type of respirators. During the time this type of respirator is worn one can stop the measurement by stopping the pump or closing the passive monitor with a cap. For all other case, the sampling must go on during wearing of respirators.

If an exposure of a SEG is not in compliance with the exposure limit, immediately the respiratory must be reviewed and improved where needed and technical measures must be considered to control exposure. If the technical measures cannot reduce exposure to an acceptable level, workers should continue to wear respirators. In that case one can measure the "**daily intake**":

Sample the most exposed task(s) for which the worker must wear adequate respirators. Calculate the daily intake by subtracting this concentration from the result of the compliance measurement result for the same job; but taking into account also the protection factor of the respirator (e.g. full face mask with A2 cartridge has a protection factor of 20). That means that the concentration measured for the specific task must be divided by 20).

Note

These "**daily intake**" measurements are not obligatory to perform. Only in some countries this kind of measurements are allowed to prove compliance with national regulations.

The policy should be to comply with an Occupational Exposure Limit (OEL) at any time. Only when this is not (yet) possible, "**daily intake**" measurements can prove that the measures (personal protection in this case) are adequate.

6.5.2 Initial monitoring

If after the *basic survey* (e.g. EN689 / 5.1.4.2 or the company specific exposure assessment methodology); an exposure profile of a SEG can not be classified as acceptable or unacceptable, initial compliance monitoring is used to assess adherence to an exposure limit. The number of measurements varies from 3 till 12 samples.

Number of measurements

- In the first step of this subsequent exposure assessment, a number of 3 measurements is enough.
- Determine at random for each SEG 3 workers in 3 non-consecutive shifts, but trying to cover all the shifts (e.g. the Day-shift of 1st week, Evening-shift of 2nd week and Night-shift of 3rd week.)
- If it appears that the mean concentration of the 3 measurements is above the 10% of the exposure limit, 9 more measurements should be performed

How to judge the results of these 12 measurements is described in **chapter 7**, "Conclusions of the assessment of occupational exposure (see also flowsheet annex 1)

6.5.3 Periodic monitoring

If after the initial monitoring, a SEG is judged as acceptable, mostly periodic measurements must be organized. The aim is to verify on a regular base if the exposure conditions didn't change and/or if technical exposure control measures are working properly.

In many countries the seasons will have some influence on the level of exposure. But also the day, evening and night-time periods within 24 hours can have considerable different exposures either due to weather changes or to work practice differences.

In case of high hazard **chronic-acting substances** like carcinogens, e.g. Vinyl chloride and 1,2-Dichloroethane, the long-term average concentration over weeks or months is a better parameter than the calculation of the probability of exceeding the exposure limit. That is why for Vinyl chloride and 1,2-Dichloroethane the measurement strategy for some exposure profiles (depending on the mean concentration) based on measurements in the 4 seasons and in the different shifts.

The **mean concentration** of the exposure profile of a SEG will define the frequency of the measurements.

Arithmetic mean concentration is < 1% of exposure limit.

For a SEG with a mean concentration of less than 10 % of the exposure limit, (more) periodic sampling is not necessary.

Arithmetic mean concentration is \geq 1% and < 10% of exposure limit,

For a SEG with a mean concentration greater or equal to 1% and lesser than 10% of the exposure limit, the following measurement strategy should be performed:

1. Establish for the SEG one day per year of monitoring, e.g. Augustus 5th.
2. Determine at random for each SEG 3 workers in 3 non-consecutive shifts, but trying to cover all the shifts (e.g. the Day-shift of 1st week, Evening-shift of 2nd week and Night-shift of 3rd week.)
3. Carry out the measurements (also if there are less working activities or there are special activities) on that specific day and shift with the at random determined worker.
4. Calculate the arithmetic mean concentration and restart the judgement of the exposure profile (on top of the flow sheet in Annex 1) and verify if the arithmetic mean concentration stays under 10% of the OEL.

Arithmetic mean concentration is \geq 10% and < 100% of exposure limit,

For a SEG with a mean concentration greater or equal to 10% and lesser than 100% of the exposure limit, the following measurement strategy should be performed:

1. Establish in every season one day of monitoring, e.g. monitor on February 5th, Mai 5th, August 5th and November 5th.
2. Determine at random for each SEG 3 workers in 3 non-consecutive shifts, but trying to cover all the shifts (e.g. the Day-shift of 1st week, Evening-shift of 2nd week and Night-shift of 3rd week.)
3. Carry out the measurements (also if there are less working activities) on that specific day and shift with the at random determined worker. But keep in mind that not the specific worker is important, but the function or activity that the worker is carrying out.
4. Calculate for the 12 measurements (for every SEG), the arithmetic mean concentration, verify if the distribution is log-normal and calculate the $UCL_{1,95\%}$ following the Land's "Exact" method and judge if the exposure is acceptable (see chapter 7).

Of course each set of 3 measurements can be evaluated on the acceptability, but for the evaluation of the long-term average, you need in this case 12 measurements.

See flow sheet annex 1.

7. CONCLUSION OF THE ASSESSMENT OF OCCUPATIONAL EXPOSURE

See also flowsheet in Annex 1

7.1 INITIAL MONITORING

1. If the mean exposure concentration is below 10% of the limit value and it can be shown that these results are representative for the long-term workplace conditions, the periodic measurements can be omitted. In such cases a regular check is required in order to verify if that conclusion is still applicable. The exposure is **acceptable**.
2. If the mean exposure concentration is above 10% of the limit value, the exposure is **uncertain**. Perform with a minimum of 12 measurements a statistic evaluation and judge if the exposure is acceptable or unacceptable.
This statistical evaluation is the same as described in 7.2 “Periodic monitoring”.
3. If the mean exposure concentration is above 100% of the limit value, the exposure is **unacceptable**.
 - The reasons for this should be identified and appropriate measures to control the overexposure should be implemented immediately.
 - It can occur that the measured shift was not a normal (normative) day. If you can make it plausible that the high concentration is not representative for normal operations, you can skip the result and take a new measurement.
 - After appropriate measures have been implemented or new measurements are done, repeat the judgment of the acceptability of the exposure profiles.

7.2 PERIODIC MONITORING

Usage of statistics in judging quantitative monitoring data

To make the decision if an exposure is acceptable, we must answer two questions:

- a) Is the SEG exposure profile adequately characterized?
- b) Is the probability that the exposure exceeds the limit low enough?

7.2.1 Judge if the exposure profile has a log-normal distribution.

If you must reject a distribution on its log-normality characteristics, it is possible that the exposure profile is not adequately characterised for this SEG. Maybe the SEG you are examining contains two or more different exposure profiles. In this case you must divide the SEG in two or more new SEGs and re-start the assessment.

7.2.2 Estimate the Upper Confidence Limit (UCL_{1,95%}) of the arithmetic mean

For chronic-acting substances as Quarts the long term average over weeks or months is a better parameter than the evaluation of the upper tail of 8 hour work shifts.

In case of chronic acting substances the dose effect is cumulative, an occasional high exposure is not critical, because it is the arithmetic average that summarizes the total mass absorbed by a person.

The Land's "exact" procedure is a good method to evaluate the mean concentration. With this method the one-side 95% Upper Confidence Limit (UCL_{1,95%}) of the arithmetic mean is calculated. If the calculated UCL_{1,95%} is below the OEL, you are at least 95% confident that the arithmetic mean exposure is less than the OEL.

For calculating the UCL_{1,95%} it is better to have 12 measurements than less!

The Land's "exact" confidence Limits only works with a log-normal distribution.

To determine the Arithmetic Mean by the Land's "exact" procedure is, the lognormal distribution model is a common proposed statistical model. A simple but effective statistical tool that is developed by members of the AIHA is available together with the book³⁾: *Strategy for Assessing and Managing Occupational Exposures; 1999*.

In annex 3 an example of a statistical evaluation is given.

Conclusions

1. If the arithmetic mean is <1% of the OEL, the exposure is **acceptable**. (**GREEN** situation), calculating the UCL is not necessary for the end conclusion.
If it can be proved that these values are representative for the long-term workplace conditions the periodic measurements can be omitted.
2. If the arithmetic mean is between 1- < 10% of the OEL, the exposure is **acceptable**. (**GREEN** situation), calculating the UCL is not necessary for the end conclusion, but still repeat the measurements periodically in a lower frequency than under point 4.
3. When the UCL_{1%, 95%} is higher than the OEL, the situation for this high hazard chemical is **unacceptable**. (**RED** situation)
The reasons for this should be identified and appropriate measures to control the overexposure should be implemented immediately.
Repeat the measurements after appropriate measures have been implemented.
4. When the UCL_{1%, 95%} is lower than the OEL and the arithmetic mean is ≥ 10% of the OEL, the situation is **acceptable** but still **Uncertain**, repeat the measurements periodically. (**ORANGE** situation)

7.2.3 Judging of Mixtures.

If exposure occurs to a mixture of Dichloro ethane and Vinyl chloride on the same day, e.g., one should evaluate the exposure to the mixture as described in **appendix C** of the TLV' and BEIs booklet ⁽⁴⁾.

- Calculate the sum of the two 8 hour's concentrations expressed as partition **of the OEL (TLV, SAEL or other limit):**

$$\frac{C_{VC}}{OEL_{VC}} + \frac{C_{DCE}}{OEL_{DCE}} = SUM$$

The judgment is the same as defined in 7.1.1 and 7.1.2 ,but for the mixture as the OEL = 1.

In table 3 an example is shown concerning an operator "Autoclave" in a VC processing plant.

Table 3

Example : Exposure to a mixture. Addition of different exposures

	Substance	Job	Duration of Shift	Measured concentration during Shift	TLV	Concentration during Shift related to TLV	Addition of different exposures
			mg/m ³	mg/m ³	mg/m ³	Conc. / OEL	C1/OEL1 + C2/OEL2
1	Vinyl chloride	Operator Autoclave	480	0.31	2.6	0,12	
2	1,2-Dichloro-ethane	Operator Autoclave	480	2.5	12.3	0,20	
3	SUM	Operator Autoclave	480				0.32

When one has calculated the sums of all other shifts one can evaluate these results with the statistical tool, but the corresponding OEL = 1.

See also example 2 in annex 3

7.2.4 How to cope with non-detectable values in a statistical evaluation?

It is a common problem for industrial hygienist to select a valid way of dealing with those samples reported to contain non-detectable values.

There are different methods that are described in literature. The Maximum Likelihood Estimation (MLE) method, the Regression method and the 2 simpler alternatives involved the substitution of the detection limit (L) by $L/2$ or $L/\sqrt{2}$.

Because not every one has a dedicated statistical evaluation program, it is recommended to use the $L/\sqrt{2}$ substitution method.

For example a detection limit of 0.1 mg/m³ gives a substitution of :

$$0.1/\sqrt{2} = 0.1/ 1.41 = 0.07 \text{ mg/m}^3.$$

8. RECORDKEEPING AND REPORTING

It is very important that all relevant information of each exposure assessment is recorded and included in a summary report.

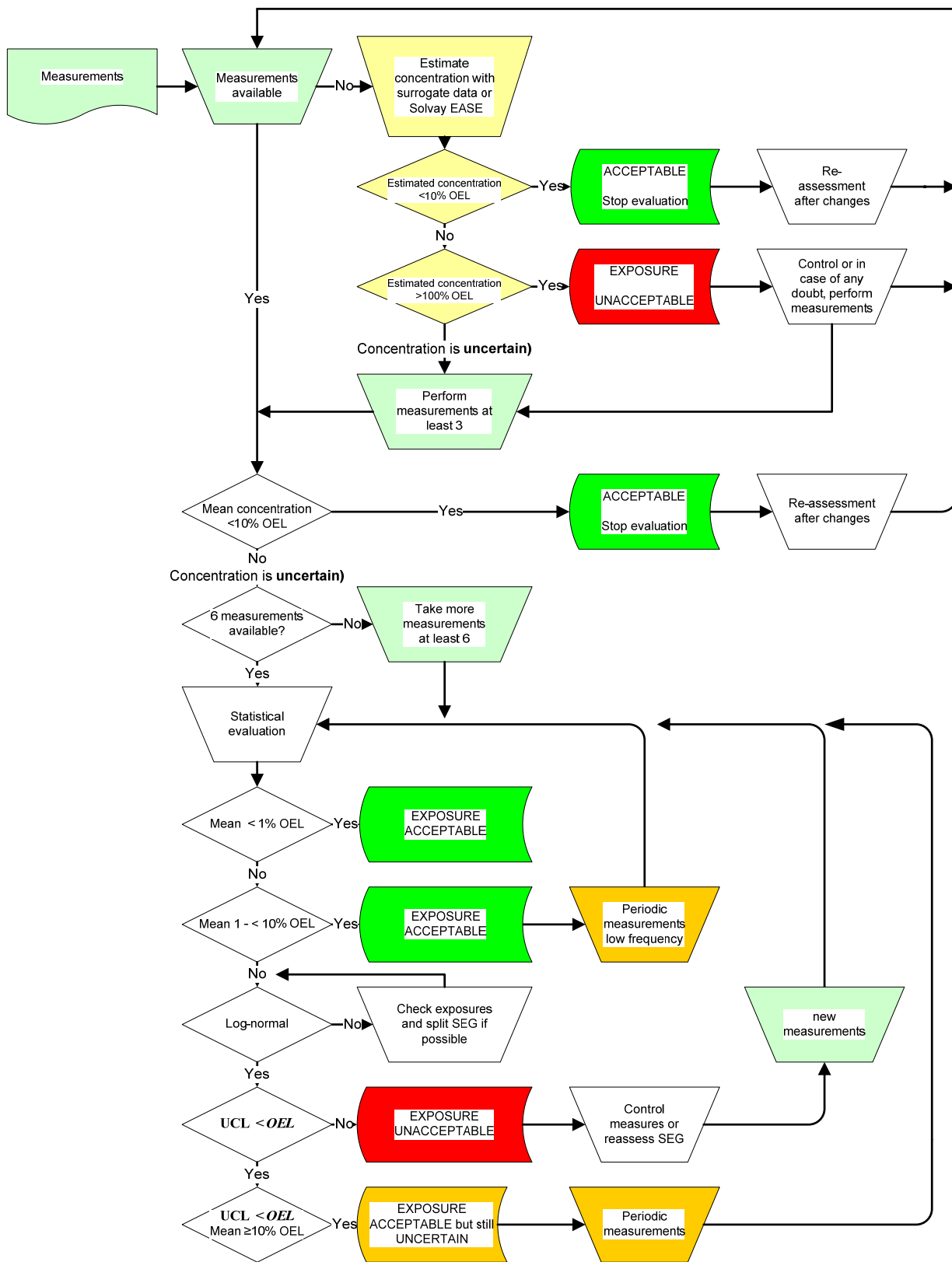
The report should contain:

- The job titles and a accurate description of the tasks undertaking the assessment and the measurements
- description of the workplace factors, including the task and process conditions during the measurements, SEG
- the sampler type and flowrate, the calibration
- sampling method (personal, fixed point)
- the measurement procedure
- the time schedule (date, start and end of sampling)
- the occupational exposure concentration
- details of quality assurance (use of blanks, ...)
- result of the comparison with the limit value
- Personal Protection Equipment (PPE) worn
- Any abnormal conditions.
- In the annex of the report: the primary analytical data as measurement time, pump velocity, total volume of air sampled, concentration Vinyl chloride and Dichloro ethane on the tubes.

A record of files (containing a wide array of relevant information) should be maintained during at least 30 years for easy retrieval of information on specific surveys and for use in epidemiological studies.

9. LITERATURE

- **EU:** European directive (89/391) "*Framework Directive on the introduction of measures to encourage improvements in the safety and health of workers at work.*"
- **CEN:** European Standard : EN 689 \ CEN
"Workplace atmospheres guidance for the assessment of exposure by inhalation to chemical agents for comparison with limit values and measurement strategy"
- **CEN:** European Standard : EN482
"Workplace atmospheres: General requirements for the performance of procedures for measurements of chemical agents", 1994
- 1) "*A collaborative European study of personal aerosol sampler performance*"
Ann. occup Hyg., Vol 41 N02. pp135-153, 1997
- 2) *Evaluation of Six Inhalable Aerosol Samplers, AJHAJ, 61:506-516*
- 3) *Strategy for Assessing and Managing Occupational Exposures; AIHA:1999*
- 4) *Adjustment of Permissible Exposure Values to Unusual Work Schedules, AIHAJ (62(September/Oktober 2001, Jules Brodeur, e.o.*
- 5) *Effect of temperature on the breakthrough of charcoal tubes during Vinyl chloride Monomer sampling, AIHAJ 61: 405-409(2000)*
- 6) *Validation of methods for the measurement of Vinyl chloride and 1,2-Dichloroethane in workplace air, NMI Reports S-CH-03-05, Th.L. Hafkenscheid, September 2003*



GLOSSARY

<i>ACGIH</i>	<i>American Conference of Governmental Industrial Hygienists</i>
<i>AIHA</i>	<i>American Industrial Hygiene Association</i>
<i>CEN</i>	<i>Comité Européen de Normalisation</i>
<i>COHYG</i>	<i>Coordinateur en Hygiène Industrielle</i>
<i>DCEa</i>	<i>1,2-Dichloroethane</i>
<i>EN</i>	<i>European Norm</i>
<i>HSE</i>	<i>Health and Safety Executive</i>
<i>ISO</i>	<i>International Organization for Standardization</i>
<i>m/s</i>	<i>meter per second</i>
<i>mg/m³</i>	<i>milligram per cubic meter</i>
<i>NIOSH</i>	<i>National Institute for Occupational Safety and Health</i>
<i>OEL</i>	<i>Occupational Exposure Limit (United Kingdom and as a common used name)</i>
<i>OSHA</i>	<i>Occupational Safety and Health Administration (US)</i>
<i>LOD</i>	<i>Limit of Detection</i>
<i>LOQ</i>	<i>Limit of Quantitation</i>
<i>NMi</i>	<i>Nederlands Meetinstituut (Institute for metrology and technology, Delft, Netherlands)</i>
<i>PEL</i>	<i>Permissible Exposure Limit (United States, OSHA)</i>
<i>PPE</i>	<i>Personal Protection Equipment</i>
<i>REL</i>	<i>Recommended Exposure Limit</i>
<i>SEG</i>	<i>Similar Exposure Group</i>
<i>TLV</i>	<i>Threshold Limit Value (United States, ACGIH)</i>
<i>TWA</i>	<i>Time Weighted Average</i>
<i>VCM</i>	<i>Vinyl chloride Monomer</i>

STATISTICAL TOOL

A simple but effective statistical tool that is developed by members of the AIHA is available together with the book *Strategy for Assessing and Managing Occupational Exposures*;3)

In this **annex** an example of statistical evaluation is given.

Example 1:

Vinyl chloride

The statistical evaluation of 12 personal 8 hours TWA measurements of Vinyl chloride in a VC production plant, **see figure 1**

The exposure limit of Vinyl chloride = 2.6 mg/m³ /1 ppm TWA 8 hours.

The concentrations are:

0.31, 0.39, 0.65, 0.75, 0.81, 0.99, 0.99, 1.07, 1.43, 1.48, 2.31, 2.47 **mg/m³**

As described before the following evaluations are important:

- Test for distribution fit: Is the exposure profile log-normal or normal.
- If yes, , the Upper Confidence Limit (UCL_{1,95%}) of the Estimated Arithmetic Mean by the Land's "Exact" procedure, must be less than the exposure limit to be acceptable

Because the substance has a high hazard chronic risk, the probability of exceeding the exposure limit doesn't give enough evidence, in this case the Upper Confidence Limit (UCL_{1,95%}) of the Estimated Arithmetic Mean by the Land's "Exact" procedure is appropriate to use.

In figure 1 of this Annex the statistical evaluation is shown of the 12 Vinyl chloride measurements.

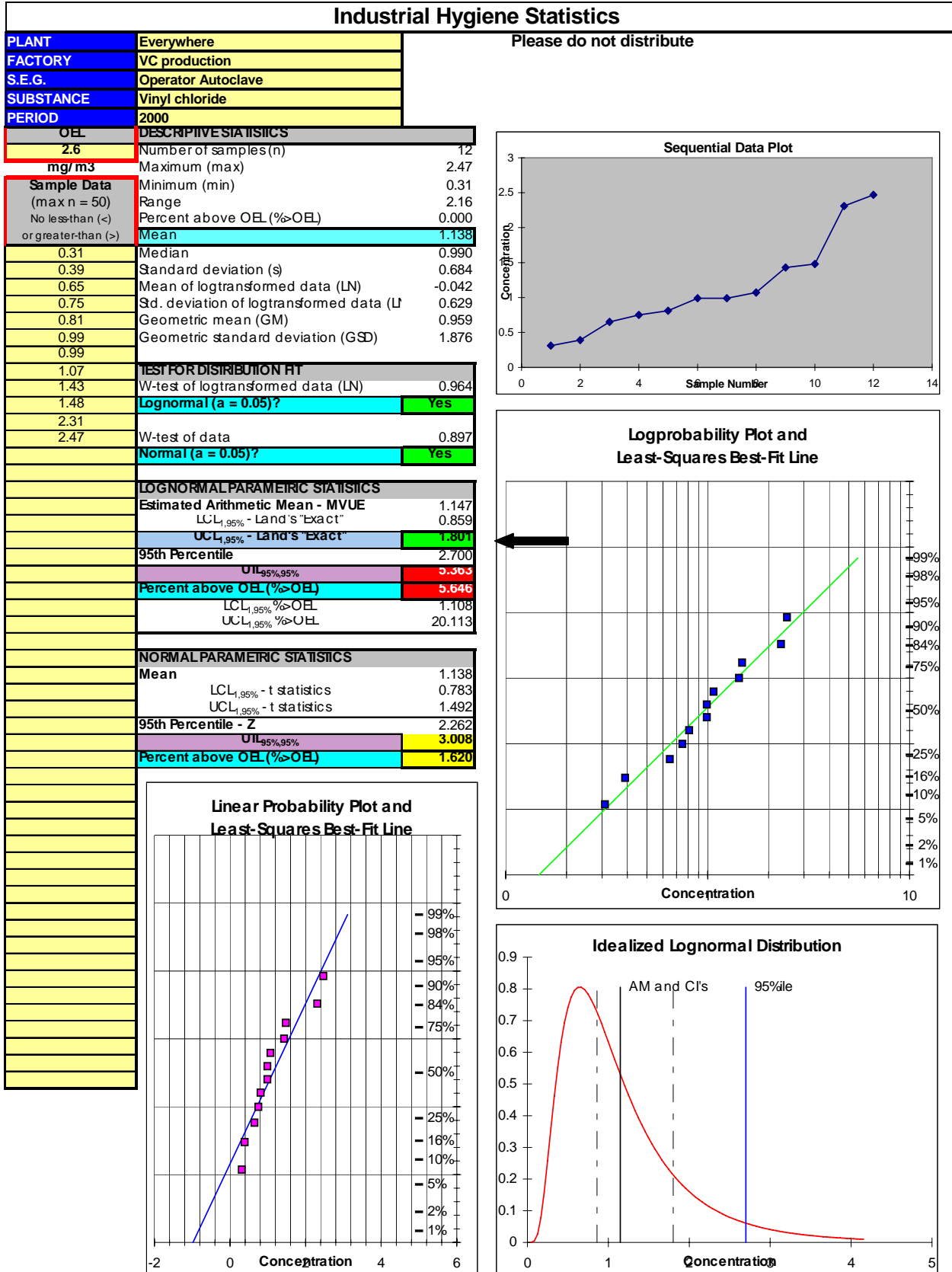
- The distribution fit is = **log-normal and normal**
- Percent above the exposure limit (% > OEL) = 5.6% = **unacceptable** (not applicable for VCM)
- Upper Confidence Limit (UCL_{1,95%}) of the Estimated Arithmetic Mean by the Land's "Exact" procedure = 1.801 mg/m³ (= < OEL of 2.6 mg/m³) = **acceptable**

End conclusion:

Because the substance has a high hazard chronic risk, the UCL_{1,95%} of the Estimated Arithmetic Mean is appropriate to use, and is in this example the exposure profile **acceptable**

Example:

Vinyl chloride. The statistical evaluation of 12 personal TWA 8 hours' measurements of Vinyl chloride in a VCM production plant.



STATISTICAL TOOL

Example 2:

Vinyl chloride + 1,2-Dichloroethane (ethylene chloride)

The statistical evaluation of 12 personal 8 hours TWA measurements of Vinyl chloride and 1,2-Dichloroethane in a VC production plant, see figure 2

The exposure limits are: Vinyl chloride (VC)= 2.6 mg/m³ and 1,2 Dichloroethane (DCE) = 12.3 mg/m³.

Because the exposure is a mixture of Dichloroethane and Vinyl chloride consecutively on one day, you can evaluate the exposure to the mixture as described in **appendix C** of the TLV' and BEI's booklet⁽⁴⁾.

- Calculate the sum of the two 8 hour's concentrations expressed as partition of the OEL (TLV, SAEL or other limit):

$$\frac{C_{VC}}{OEL_{VC}} + \frac{C_{DCE}}{OEL_{DCE}} = SUM$$

The results of the summations are:

VC	0.31	0.39	0.65	0.75	0.81	0.99	0.99	1.07	1.43	1.48	2.31	2.47	mg/m ³
	0.12	0.15	0.25	0.29	0.31	0.38	0.38	0.41	0.55	0.57	0.89	0.95	VC/TLV
DCE	2.50	3.40	1.80	5.70	6.40	2.50	7.30	2.90	4.80	2.60	1.10	0.10	mg/m ³
	0.20	0.28	0.15	0.46	0.52	0.20	0.59	0.24	0.39	0.21	0.09	0.01	DCE/TLV
SUM	0.32	0.43	0.40	0.75	0.83	0.58	0.97	0.65	0.94	0.78	0.98	0.96	VC + DCE

The judgment of the sums of different shifts is the same as with the real concentrations, but use in this case as OEL = 1.

As described before the following evaluations are important:

- Test for distribution fit: Is the exposure profile log-normal or normal.
- If yes, the Upper Confidence Limit (UCL_{1,95%}) of the Estimated Arithmetic Mean by the Land's "Exact" procedure, must be less than the exposure limit to be acceptable the percent above the exposure limit (% > OEL) must be less than 5% to be acceptable.

Because both substances have a high hazard chronic risk, the probability of exceeding the exposure limit doesn't give enough evidence, in this case the Upper Confidence Limit (UCL_{1,95%}) of the Estimated Arithmetic Mean by the Land's "Exact" procedure, is appropriate to use.

In figure 2 of this Annex the statistical evaluation is shown of the summations.

- The distribution fit is = **log-normal and normal**
- Percent above the exposure limit (% > OEL) = 15.28% = **unacceptable** (not applicable for VC/ DCE)
- Upper Confidence Limit (UCL_{1,95%}) of the Estimated Arithmetic Mean by the Land's "Exact" procedure = 0.913 ppm (= < 1 ppm) = **acceptable**

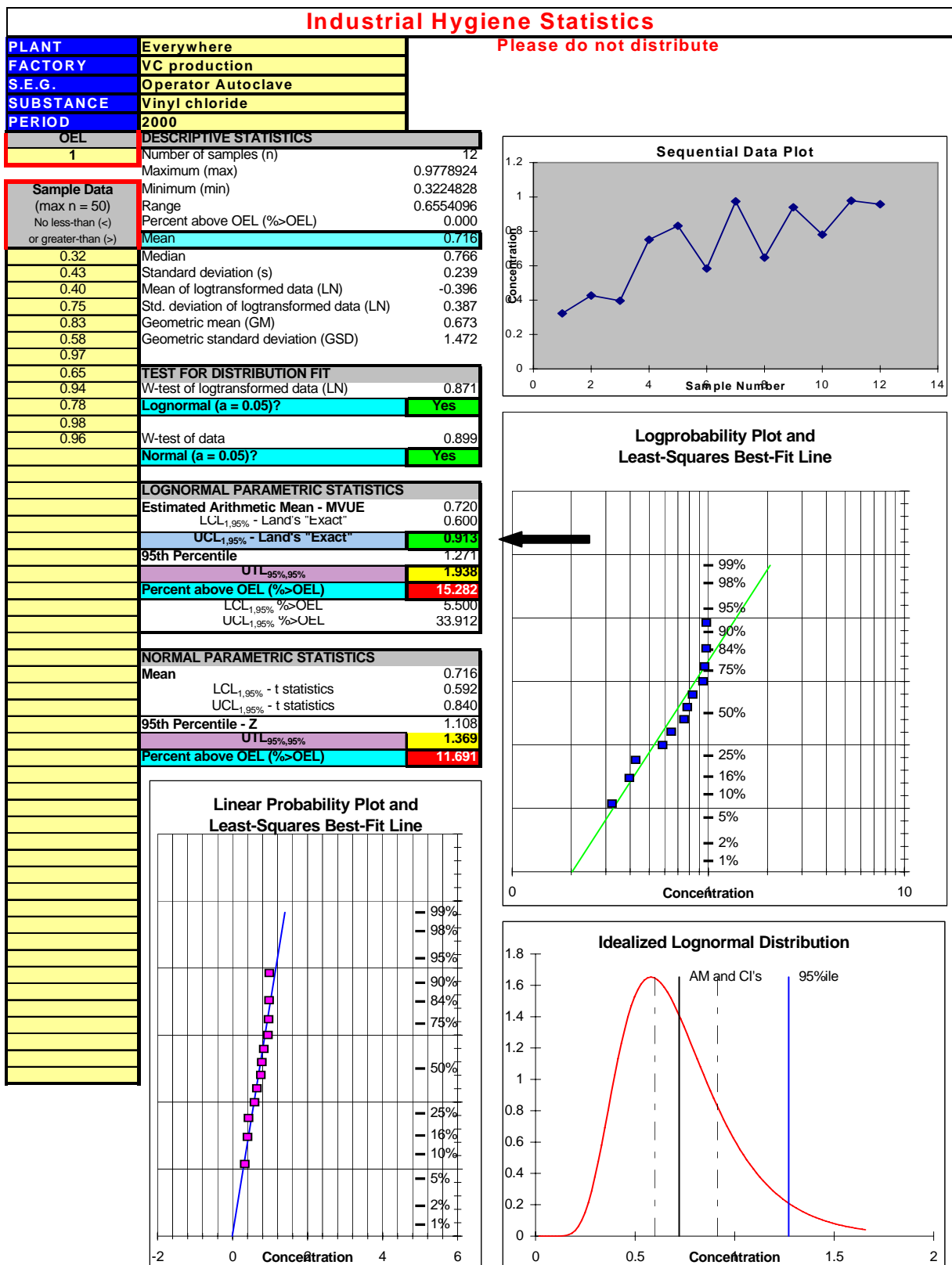
End conclusion:

Because the substance has a high hazard chronic risk, the UCL_{1,95%} of the Estimated Arithmetic Mean is appropriate to use, and is in this example the exposure profile **acceptable**

Example 2:

Vinyl chloride + 1,2 Dichloro ethane

The statistical evaluation of 12 personal 8 hours TWA measurements of Vinyl chloride and 1,2 Dichloro ethane in a VC production plant



NMi Report S-CH-03-05

**VALIDATION OF METHODS FOR THE MEASUREMENT OF VINYL CHLORIDE
AND 1,2-DICHLOROETHANE IN WORKPLACE AIR**

Author: Th.L. Hafkenscheid
Date: September 2003

AUTHENTICATION

Name and address of the sponsor
European Council of Vinyl Chloride Manufacturers

Names and functions of NMi personnel involved

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A. Baldan	Scientist
Th.L. Hafkenscheid	Project coordinator

Period in which the work reported was performed

September 2002 – April 2003

Signature

Th.L. Hafkenscheid
Project coordinator

Summary

A number of methods for the measurement of exposure of workers to vinyl chloride monomer (VCM) and 1,2-dichloroethane (DCE) have been tested for their performances under laboratory conditions. The methods include

- Pumped sampling on activated charcoal followed by desorption with carbon disulfide and analysis by gas chromatography with flame-ionization detection
- Pumped sampling on different carbon molecular sieves or porous polymer sorbents followed by thermal desorption and analysis by gas chromatography with flame-ionization detection
- Diffusive sampling on activated charcoal badges followed by desorption with carbon disulfide and analysis by gas chromatography with flame-ionization detection
- Diffusive sampling on different carbon molecular sieves or porous polymer sorbents followed by thermal desorption and analysis by gas chromatography with flame-ionization detection.

Typical sampling times are between 6 and 8 hours, concentration levels studied were 0,1 and 2 ppm(volume/volume). Tests were typically performed at 20 °C and 50% relative air humidity.

The experiments performed were based on the methodologies described in European Norms EN 482, 838 and 1076. For each method experiments were limited to those that would lead to new information; it was agreed that performance characteristics known from other studies, e.g., as performed within the frame of validating existing methods for VCM and DCE, would not be redetermined.

The results of the experiments were the following.

- Pumped sampling on activated charcoal fulfills the performance criteria given in EN 482 under all conditions studied
- Pumped sampling in combination with thermal desorption was found only to give satisfactory results for DCE sampled on Chromosorb 106; for VCM long-term sampling invariably led to incomplete recoveries on analysis.
- Diffusive sampling in combination with thermal desorption gave satisfactory results; effective uptake rates determined for VCM on Unicarb and DCE on Chromosorb 106 fulfill the performance criteria of EN 482. For VCM sampled on Unicarb, the effects of increased temperature and relative humidity are significant, however, leading to an average effective uptake rate that only just fulfills the 'overall uncertainty' criterion of EN 482.
- Diffusive sampling on charcoal badges are acceptable for DCE when using both single-layer (3M 3500) and double-layer (3M 3520) badges. For VCM; when using the single-layer badge (3M 3500) the effective uptake rate varies largely with concentration, temperature and relative humidity. Experiments with the 3M 3520 badge show a 40% decrease in effective uptake rate from 0,1 to 2 ppm concentration levels. The use of this sampler for VCM is not recommended.

Overview of the results

Desorption	Pumped sampling				Diffusive sampling				Comments
	CS ₂		Thermal		CS ₂		Thermal		
	VCM	DCE	VCM	DCE	VCM	DCE	VCM	DCE	
Activated charcoal tube	Yes	Yes							
Chromosorb 106				Yes				Yes	
Unicarb			No	No			Yes	Yes	
Carbosieve III			No	No			No	No	
Activated charcoal badge 3M 3500					No	Yes			
Activated charcoal badge 3M 3520					No	Yes			

Yes = method fulfills the performance criteria given in EN 482, 838 and/or 1076

1. INTRODUCTION

Vinyl chloride monomer (VCM) and 1,2-dichloroethane (DCE) are recognized human carcinogens on exposure via inhalation. Monitoring of exposure concentrations is an essential element of the protection of workers that are potentially exposed to these compounds. For this purpose a number of methods can be applied that are combinations of pumped or diffusive sampling with analysis by gas chromatography after either solvent desorption or thermal desorption.

Current concentration levels that are of interest range around limit values of 1 ppm for both compounds.

For the relevant concentration ranges (about 0,1 to 2 ppm) no validation data are available that would be fully appropriate to Euronorms 482, 838 and 1076 [1-3].

For this reason, the European Council of Vinyl Chloride Manufacturers (ECVM) has requested NMI to perform validation studies for the methods most appropriate to the measurement of exposure to VCM and DCE in the aforementioned concentration ranges. The experiments would be performed in order to obtain 'missing' data for performance characteristics, knowing that information for some characteristics such as stability on activated charcoal is already available, e.g., from existing measurement protocols [4-12].

The methods selected for validation were:

- pumped sampling on standard activated charcoal tubes followed by desorption with carbon disulfide
- pumped sampling on carbon molecular sieve-based sorbent tubes followed by thermal desorption
- diffusive sampling on 3M charcoal badges followed by desorption with carbon disulfide
- diffusive sampling on carbon molecular sieve-based sorbent tubes followed by thermal desorption.

This report describes the methodology used in and results of the validation study.

2. EXPERIMENTAL

2.1 Chemicals and materials

2.1.1 Chemicals

- VCM of 99.5+% purity was supplied by Aldrich.
- DCE of 99.8% purity was supplied by Janssen Chimica.
- Carbon disulfide of 99.9% purity by Promochem (LGC)
- n-Hexane of 99.7+% purity by Fluka (internal standard for samples desorbed with carbon disulfide)
- Water used for humidification of the air was purified using a Milli-Q purification unit (Millipore).

2.1.2 Materials

- Nitrogen, used as purge gas, grade 5.0, with additional purification using a Supelco air purifier.
- Zero air, generated from ambient air by drying and subsequent removal of impurities (MCZ K-100 Air Purification system).
- Of VCM, a gas mixture of 2.00 % (mol/mol) in nitrogen has been prepared by gravimetry (ISO 6142).
- Standard sample tubes containing 400+200 mg activated coconut charcoal were supplied by Koenders.

Annex 4:

- Sample tubes for thermal desorption, dimensions 3.5 inch length, 0.25 inch outer diameter, 5 mm inner diameter, containing
 - 200 mg Tenax TA
 - 300 mg Chromosorb 106 (C106),
 - 300 mg Unicarb, (Unic.), or
 - 300 mg Carbosieve SIII (CS3) each,were supplied by Markes International.

Tubes were conditioned prior to use by purging for 100 minutes at 300 °C (225 °C for Chromosorb 106) with 30 ml/min of purified helium.

- Activated charcoal sample badges (3M types 3500 and 3520) were supplied by Zeeland Support.
- Uncoated fused-silica tubing, 75 µm and 0.53 mm internal diameter, was supplied by Chrompack.

2.2 Equipment

2.2.1 Mass-flow controllers

Mass-flow controllers of various ranges for setting and controlling the flows of air, VCM gas mixture and nitrogen (Bronkhorst HiTec).

2.2.2 Flow meters

For the setting of flow rates calibrated NMI-made mercury-piston flowmeters, and a BIOS DryCal flow meter, calibrated against the mercury-piston flow meters, were used.

2.2.3 Glassware

Borosilicate tubing and mixing vessels with Rotulex connections and Schott GL sampling ports for the assembly of the dilution part of the generation unit.

2.2.4 Continuous injection unit for the preparation of standard atmospheres

For the preparation of the standard atmospheres of DCE according to ISO 6145 part 4, a self-constructed capillary dosage unit was used.

2.2.5 Gas chromatographs (GC)

Two Perkin-Elmer Autosystem XL gas chromatographs, equipped with a flame-ionisation detector (FID). One of these (System 1) is equipped with a split/splitless injector, the other (System 2) with an automated thermal desorber. Separation of components was effected using a 30 m fused-silica capillary column, with internal diameter of 0.32 mm, with a 5 µm CP-Sil 5 CB stationary phase (System 1) or a 25 m fused-silica capillary column, with internal diameter of 0.32 mm, with a 1.2 µm CP-Sil 13 CB stationary phase (System 2).

2.2.6 Automated thermal desorber (ATD)

Perkin Elmer ATD 400, equipped with a 30 mg Tenax TA cold trap unit.

2.2.7 Data acquisition and handling software

Perkin Elmer Turbochrom Workstation version 6.1.0

2.2.8 Automated gas chromatograph

Synspec 955 gas chromatograph equipped with a PID detector for continuous monitoring of generated standard atmospheres.

2.2.9 Balance

Mettler AT 201 balance, readable to 10 micrograms (µg).

Annex 4:

2.2.10 *Water vapour generation unit*

Water vapour was generated using a liquid mass-flow controller (Bronkhorst HiTec), operated by applying a small pressure using purified helium from a 2.5-litre Schott flask. The water was vaporized using a modified Miller-Nelson Inc. SV-20 vaporizer.

2.2.11 *Temperature and relative humidity (RH) measurement*

Continuous measurements of air temperature were effected using a thermocouple with continuous logging. Relative humidities were measured using a Vaisala HMI33 relative humidity/temperature meter equipped with a HMP31UTL sensor. The reading of the RH sensor was checked before use at 0 and 100% RH.

2.3 *Calibration standards*

2.3.1 *Solvent desorption*

Solutions of VCM and DCE in carbon disulfide were prepared by gravimetry by adding known masses of VCM or DCE to carbon disulfide and subsequent gravimetric dilution of the stock standards.

2.3.2 *Thermal desorption*

Preconditioned sorbent tubes were spiked with known amounts of the compounds under investigation by sampling known volumes of a standard atmosphere generated using dynamic blending (VCM) or continuous injection (DCE).

2.4 *Generation of standard atmospheres*

Standard atmospheres were generated

- From a 2% gas mixture of VCM in nitrogen by dynamic blending
- From DCE by continuous injection and subsequent vaporization of the pure compound.

For the high levels one-stage dilution was used; for the low levels a two-stage dilution was used.

During the generation, the constancy of the concentrations was checked using the automated gas chromatograph.

The uncertainty in the concentrations generated is a function of the uncertainties in

- component purities (always >99,5%)
- dosage rate
- main dilution air flow rate
- air temperature and pressure during the experiments (NB. knowledge of average air temperature and pressure is required for the conversion of concentrations from mass per volume to dimensionless units).

The standard uncertainty in the average concentrations, determined by combination of experimentally assessed uncertainties, is estimated to be $\pm 2\%$, giving an expanded uncertainty of $\pm 4\%$ (corresponding to 95% confidence limits).

2.5 *Pumped sampling from standard atmospheres*

In each experiment, 6 samplers were loaded simultaneously using an NMI-constructed sampling manifold. Sampling was effected by mass-flow controllers, calibrated before each experiment using calibrated flow meters (2.2.2). After sampling, samples were stored under appropriate conditions before analysis.

2.6 *Diffusive sampling from standard atmospheres*

In each experiment, 6 samplers of each sorbent were exposed simultaneously to the standard atmospheres by placing them in a modified reaction vessel through which the standard atmosphere was passed upwards at a linear velocity of approximately 30 cm/s (3M samplers) or 2 cm/s (tube samplers).

2.7 *Analysis of standards and samples*

Standards and samples were analysed under the following conditions.

Annex 4:

System 1

<i>Desorption conditions</i>		<i>GC settings</i>	
Volume of carbon disulfide for tubes	≈ 3 mL for active charcoal samples and 1,5 mL for 3M determined by weighing	Detector temperature (°C)	300
		Column temperature initial (°C)	35
		Hold time (min)	1
		Temperature program rate 1 (°C/min)	15
Internal standard	n-Hexane	Column temperature 2 (°C)	95
		Hold time (min)	1

System 2 for diffusive samplers

<i>ATD-settings</i>		<i>GC settings</i>	
Sample desorption temperature (°C)	190 for C106 300 for Unicarb, CS3	Detector temperature (°C)	350
Desorption flow (mL/min)	30	Column temperature initial (°C)	35
Desorption time (min)	2,5	Hold time (min)	5
Cold trap low temperature (°C)	-30	Temperature program rate 1 (°C/min)	25
Cold trap high temperature (°C)	225	Column temperature 2 (°C)	160
Trap hold time (min)	1	Hold time (min)	0
Outlet split (mL/min)	20		

System 2 for pumped samplers

<i>ATD-settings</i>		<i>GC settings</i>	
Sample desorption temperature (°C)	190 for C106 300 for Unicarb, CS3	Detector temperature (°C)	350
Desorption flow (mL/min)	30	Column temperature initial (°C)	35
Desorption time (min)	7	Hold time (min)	5
Cold trap low temperature (°C)	-30	Temperature program rate 1 (°C/min)	25
Cold trap high temperature (°C)	225	Column temperature 2 (°C)	160
Trap hold time (min)	1	Hold time (min)	0
Outlet split (mL/min) *	150-350		

* Different outlet split values were used depending on the amount of volume collected

3 RESULTS AND DISCUSSION

3.1 Pumped sampling, solvent desorption

3.1.1 Desorption efficiency

The desorption efficiency (DE) of the charcoal tubes was determined for VCM and DCE at 5 loading levels each by comparison of levels determined by analysis with loading levels calculated from standard atmosphere concentrations and sample volumes. For each level 3 tubes were loaded and the desorbates analyzed in triplicate. The results for each concentration level (mean DE \pm standard deviation) are given in Table 1 below as the

Table 1. Desorption efficiencies of charcoal tubes

VCM		DCE	
Loading (μg)	DE (%)	Loading (μg)	DE (%)
25	85 \pm 4	41	95 \pm 1
50	90 \pm 1	82	91 \pm 2
75	89 \pm 1	122	87 \pm 1
100	90 \pm 1	163	88,0 \pm 0,3
125	90 \pm 1	204	89,2 \pm 0,4

From these results it may be concluded that over the loading ranges studied, the desorption efficiencies fulfill the criterion set in EN 1076 [3], i.e., DE \geq 75%, with a relative standard deviation \leq 10%.

3.1.2 Recoveries of VCM and DCE

Recoveries of VCM and DCE were determined at 2 concentration levels and 2 sample flow rates.

Concentration levels studied were approximately 0,1 and 2 ppm, sample flow rates were 25 and 50 mL/min, sampling time was 8 hours (i.e., 12 and 24 L sample volumes). The results are given in Tables 2-5 below as the mean \pm standard deviation of the analysis of 6 samples each.

Table 2. Recoveries of VCM and DCE: 0,1 ppm, 25 mL/min, 8 h

VCM				DCE			
Target (μg)	Found (μg)	Recovery (%)	OU (%) [1]	Target (μg)	Found (μg)	Recovery (%)	OU (%) [1]
3,1	3,4 \pm 0,1	110 \pm 2	14 %	5,1	4,8 \pm 0,4	95 \pm 9	23

Table 3. Recoveries of VCM and DCE: 0,1 ppm, 50 mL/min, 8 h

VCM				DCE			
Target (μg)	Found (μg)	Recovery (%)	OU (%) [1]	Target (μg)	Found (μg)	Recovery (%)	OU (%) [1]
6,2	6,8 \pm 0,1	110 \pm 2	14 %	10,0	9,4 \pm 0,4	94 \pm 5	16

Table 4. Recoveries of VCM and DCE: 2,0 ppm, 25 mL/min, 8 h

VCM				DCE			
Target (μg)	Found (μg)	Recovery (%)	OU (%) [1]	Target (μg)	Found (μg)	Recovery (%)	OU (%) [1]
62	61 \pm 0,6	98 \pm 1	4 %	99	91 \pm 2	91 \pm 2	13

Table 5. Recoveries of VCM and DCE: 2,0 ppm, 50 mL/min, 8 h

VCM				DCE			
Target (μg)	Found (μg)	Recovery (%)	OU (%) [1]	Target (μg)	Found (μg)	Recovery (%)	OU (%) [1]
124	122 \pm 3	98 \pm 2	6 %	197	186 \pm 2	95 \pm 1	7

For each of the conditions studied, the criteria given in EN 482 [1] for the 'overall uncertainty' (OU = bias + 2 times standard deviation \leq 50% for the level of 0,1 ppm or \leq 30% for the level of 2 ppm) are amply fulfilled, indicating the fitness for purpose of the pumped sampling – solvent desorption method.

3.2 Pumped sampling, thermal desorption

Recoveries of VCM and DCE were determined at approximately 0,1 and 2 ppm. Several sample flow rates were applied for 8h sampling: 20, 25 and 50 mL/min. The results of the analyses for VCM and DCE on carbon molecular sieves revealed a high variability, indicating the methodology not to be robust. For DCE sampled on Chromosorb results are more consistent.

Results obtained for 8-h sampling at a flow rate of 20 mL/min are given in table 6-7, expressed as the mean \pm standard deviation of the analysis. The results of all experiments are given in Annex 1.

Table 6. Results for VCM

Sorbent	Conc. (ppm)	Sample flow (mL/min)	Sampling time (min)	Target (μ g)	Found (μ g)	Recovery (%)	OU (%)
Unicarb	0,1	20	480	2,5	1,7 \pm 0,2	69 \pm 7	50
Carbosieve SIII	0,1	20	480	2,5	0,4 \pm 0,2	15 \pm 8	192
Unicarb	2	20	480	48	18 \pm 3	38 \pm 5	91
Carbosieve SIII	2	20	480	48	9,1 \pm 1,7	18 \pm 3	120

Table 7. Results for DCE

Sorbent	Conc. (ppm)	Sample flow (mL/min)	Sampling time (min)	Target (μ g)	Found (μ g)	Recovery (%)	OU (%)
Chromosorb 106	0,1	20	480	4,1	3,8 \pm 0,2	92 \pm 4	18
Chromosorb 106	2	20	480	84	74 \pm 3	88 \pm 3	22

Recoveries and overall uncertainties for DCE at the two concentration levels are acceptable at this sample flow rate. Very low recoveries and large overall uncertainties are found for VCM, in particular for Carbosieve III sorbent tubes. Apparently the low VCM recoveries are due to incomplete desorption of the loaded mass on analysis. Further studies are necessary to establish more appropriate analytical conditions of analysis, if any.

In addition, the sample stability was determined for VCM on Unicarb samplers after 2 weeks of storage at room temperature. The results are given in Table 8.

Table 8. 2-week stability of VCM on Unicarb

μ g VCM found, t=0	μ g VCM found, t=2 weeks	Recovery after 2 weeks storage
1,7 \pm 0,2	1,7 \pm 0,2	96,5 %
18 \pm 3	19 \pm 1	105 %

Within the experimental limitations discussed above, VCM sorbed on Unicarb samplers is found to be stable when stored for 2 weeks at room temperature.

3.3 Diffusive sampling, solvent desorption

3.3.1 Determination of effective uptake rates

The effective uptake rates were first determined for the 3M 3500 diffusive sampler at concentration levels of 0,1 and 2 ppm during 8 hours exposure at 20 °C and 50% relative humidity.

In addition, the effective uptake rate was determined under 'extreme' conditions of 30 °C and 90% relative humidity.

The effective uptake rates for the 3M 3500 sampler are given in Table 9 below as the mean \pm standard deviation of 6 samplers each. These uptake rates have been calculated without correcting for desorption efficiencies.

Table 9. Effective uptake rates for the 3M 3500 sampler

Temperature (°C)	Relative humidity (%)	Concentration (ppm)		Effective uptake rate (mL/min)	
		VCM	DCE	VCM	DCE
20,5	48	0,10	0,10	35 \pm 6	30 \pm 1
21,5	49	2,0	2,0	20 \pm 2	28,9 \pm 0,5
30,4	88	2,0	2,0	9 \pm 2	28 \pm 1

The effective uptake rate for DCE is found not to vary significantly under the above conditions. By combination of the uptake rates determined, taking into account the uncertainty in the concentrations of the standard atmospheres generated, the mean effective uptake rate for DCE is 29,1 mL/min \pm 8% (95-% confidence limits). The effective uptake rate given by the manufacturer [12], corrected for recovery, is 32,4 mL/min, indicating a bias of -10 % in the concentration calculated when using the manufacturer's uptake rate. The overall uncertainty [1] for the sampler - based on manufacturer's data - would be 18%. Hence, the sampler fulfills the criteria given in [1].

From the experimental results it is evident that the 3M 3500 sampler cannot be used for VCM. Because of the apparent invalidity of the 3M 3500 sampler for VCM, the experiments for VCM were partly repeated using the 3520 sampler. These experiments were not included in the original project plan. The results are given in Table 10 below.

Table 10. Effective uptake rates of 3M 3520 sampler

Temperature (°C)	Relative humidity (%)	Concentration (ppm)		Effective uptake rate (mL/min)	
		VCM	DCE	VCM	DCE
19,8	48	0,10	0,10	47 \pm 3	32 \pm 1
19,7	48	2,0	2,0	33 \pm 1	29 \pm 1

The results for DCE are again satisfactory; for VCM a significant decrease in effective uptake rate is noted with increasing concentration.

3.4 Diffusive sampling, thermal desorption

3.4.1 Determination of effective uptake rates

The effective uptake rates were first determined for Perkin Elmer-type diffusive samplers with sorbents Carbosieve SIII (C S3), Unicarb or Chromosorb 106 (C 106), at concentration levels of 0,1 and 2 ppm during 8 hours exposure at 20 °C and 50% relative humidity.

In addition, the effective uptake rate was determined under 'extreme' conditions of 30 °C and 90% relative humidity.

The effective uptake rates for the samplers are given in Table 11 below as the mean \pm standard deviation of 6 samplers each.

Table 11. Effective uptake rates for the Perkin Elmer sampler

Temperature (°C)	Relative humidity (%)	Concentration (ppm)		Effective uptake rate (ng/ppm.min)			
		VCM	DCE	VCM		DCE	
				C S3	Unicarb	Unicarb	C 106
20,5	48	0,10	0,10	1,14 \pm 0,07	1,38 \pm 0,05	1,33 \pm 0,13	2,17 \pm 0,05
21,5	49	2,0	2,0	1,08 \pm 0,02	1,36 \pm 0,03	1,67 \pm 0,04	2,01 \pm 0,03
30,4	88	2,0	2,0	0,90 \pm 0,10	1,01 \pm 0,06	1,34 \pm 0,14	1,86 \pm 0,03

For these samplers, no literature information is available for calculation of the overall uncertainty. Hence, the results for each experiment were compared (t-test); at the 95% confidence level, only the results for VCM on Unicarb at the 2 ppm level ('normal' vs. 'extreme' conditions) were found to be statistically significantly different. No significant effect was seen when increasing the concentration from 0,1 to 2 ppm, although the increase in uptake rate for DCE on Unicarb is somewhat surprising.

Estimated mean effective uptake rates and uncertainties (95% confidence level) were obtained for each sorbent and compound from the extreme uptake rates found and experimental uncertainties reflected by the standard deviations of the effective uptake rates (Table 11). The resulting mean uptake rates and uncertainties are given in Table 12.

Table 12. Effective uptake rates (ng/ppm.min) and relative uncertainties for the Perkin Elmer sampler

VCM		DCE	
Carbosieve SIII	Unicarb	Unicarb	Chromosorb 106
1,02 \pm 38 %	1,25 \pm 30%	1,50 \pm 17 %	2,01 \pm 15%

From these data it can be observed that all combinations except VCM sampled on Carbosieve SIII fulfill the overall uncertainty criterion of [1] for the concentration range of 0,1 to 2 times the limit value.

4 CONCLUSIONS

A number of methods for the measurement of exposure of workers to vinyl chloride monomer (VCM) and 1,2-dichloroethane (DCE) have been tested for their performances under laboratory conditions.

Typical sampling times are between 6 and 8 hours, concentration levels studied were 0,1 and 2 ppm(volume/volume). Tests were performed at 20 °C and 50% relative air humidity and at 30 °C and 80-90% relative air humidity.

The conclusions from the experiments are the following.

Pumped sampling on activated charcoal with carbon disulfide desorption

The method fulfills the performance criteria given in EN 482 and EN 1076.

Desorption efficiencies were generally 90% or better.

The criteria for 'overall uncertainty' were fulfilled under all conditions studied, for sample volumes of 12 and 24 liters.

Pumped sampling with thermal desorption

The methodology was found to give unsatisfactory results in all cases, although for DCE sampled on Chromosorb 106 the 'overall uncertainty' always fulfilled the uncertainty criterion of EN 482.

The desorption efficiency, however, was < 95%.

For VCM long-term sampling invariably led to incomplete recoveries on analysis, resulting in violations both of the uncertainty and desorption efficiency criteria of EN 482 and EN 1076.

Diffusive sampling with thermal desorption

The methodology gives satisfactory results; effective uptake rates determined for VCM on Unicarb and DCE on Chromosorb 106 fulfill the performance criteria of EN 482. For VCM sampled on Unicarb, the effects of increased temperature and relative humidity are significant, however, leading to an average effective uptake rate that only just fulfills the 'overall uncertainty' criterion of EN 482.

Diffusive sampling on activated charcoal badges

Results are acceptable for DCE when using both single-layer (3M 3500) and double-layer (3M 3520) badges. For VCM; when using the single-layer badge (3M 3500) the effective uptake rate varies largely with concentration, temperature and relative humidity. Experiments with the 3M 3520 badge show a 40% decrease in effective uptake rate from 0,1 to 2 ppm concentration levels. The use of this sampler for VCM is not recommended. .

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ANNEX 1. FULL RESULTS FOR PUMPED SAMPLING / THERMAL DESORPTION*Results for VCM*

<i>Sorbent</i>	<i>Conc. (ppm)</i>	<i>Sample flow (mL/min)</i>	<i>Sampling time (min)</i>	<i>Target (µg)</i>	<i>Found (µg)</i>	<i>Recovery (%)</i>	<i>OU (%)</i>
<i>Unicarb</i>	0,1	20	480	2,5	1,7 ± 0,1	67 ± 4	46
<i>Unicarb</i>	0,1	20	480	2,5	1,6 ± 0,1	65 ± 4	52
<i>Unicarb</i>	0,1	20	480	2,5	1,7 ± 0,2	69 ± 7	50
<i>Carbosieve SIII</i>	0,1	20	480	2,5	0,4 ± 0,2	15 ± 8	192
<i>Unicarb</i>	2	20	480	48	18 ± 3	38 ± 5	91
<i>Carbosieve SIII</i>	2	20	480	48	9,1 ± 1,7	18 ± 3	120
<i>Unicarb</i>	2	25	360	46	42 ± 1	91 ± 2	13
<i>Carbosieve SIII</i>	2	25	480	62	47 ± 1	75 ± 1	31
<i>Unicarb</i>	2	50	360	93	69,5 ± 0,1	74,8 ± 0,1	25
<i>Carbosieve SIII</i>	2	50	480	123	72 ± 3	58 ± 2	50

Results for DCE

<i>Sorbent</i>	<i>Conc. (ppm)</i>	<i>Sample flow (mL/min)</i>	<i>Sampling time (min)</i>	<i>Target (µg)</i>	<i>Found (µg)</i>	<i>Recovery (%)</i>	<i>OU (%)</i>
<i>Chromosorb 106</i>	0,1	20	480	4	3,0 ± 0,1	77 ± 2	30
<i>Chromosorb 106</i>	0,1	20	480	4,1	3,8 ± 0,2	92 ± 4	18
<i>Chromosorb 106</i>	2	20	480	84	74 ± 3	88 ± 3	22
<i>Chromosorb 106</i>	2	20	480	80	63 ± 3	78 ± 3	30
<i>Unicarb</i>	2	25	360	73	28 ± 2	38 ± 2	74
<i>Carbosieve SIII</i>	2	25	480	98	23 ± 3	24 ± 3	57
<i>Unicarb</i>	2	50	360	148	67 ± 1	45 ± 4	102
<i>Carbosieve SIII</i>	2	50	480	195	67 ± 14	34 ± 7	109