Hazardous substances in freight containers
Requirements concerning measurements and assessments

Experience gained during the customs clearance of all types of import freight03, container in Hamburg has shown some 20% to be contaminated with considerable concentrations of hazardous substances in the breathing air. This applies not only to hazardous freight, but to cargoes of all kinds, which may:

- have been fumigated in order to protect against pests;
- continue to emit gases from the manufacturing process;
- have been treated following manufacture in order to prevent mould.

Some harmful substances are odourless or their odour is masked by other odours. Measurements must therefore be performed in order to exclude hazards. Fumigated containers are however subject to mandatory marking.

Persons may be particularly exposed to hazards when containers are first opened, during inspection of their contents, and during the unloading of their cargoes. Should the exposure to hazardous substances be high, the container must be adequately ventilated before it is entered. If the presence of fumigating agent is suspected, the container may first have to be released by a fumigation expert.

With the support of experts from measurement institutes and fumigation companies, the Hamburg Occupational Health and Safety Office and ZfAM (the central institute of occupational medicine and maritime medicine in Hamburg) have formulated minimum requirements governing the assessment of import freight containers. The requirements cover the sampling parameters, substances to be analysed, analysis methods, and the limit, guide and intervention values which are to be employed as reference values. The intervention values stated address typical work situations during the unloading of containers and are not suitable for use as limit values in other work situations.

The minimum requirements provide the labour inspectorates and chemical laboratories with an indication of the nature and scale of the assessment and of the measures which may be necessary. Based upon the assessments, the recipients of containers are better able to identify hazards to the environment and to perform risk assessments in accordance with the German Occupational Health and Safety Act and the Dangerous Chemicals Regulation.

The assessment must be such that it can be interpreted easily and unambiguously by the commissioning party. For this purpose, the measured values are compared to reference values. From the quotient of the measured value and the reference value, referred to as the assessment index, the relevance of individual parameters within the complex measurement results can quickly be determined. The assessment should provide clear information on ventilation and further protective measures, including for similar cases in the future. The assessment enables parties ordering imports or recipients of the import freight containers to exert direct influence upon their importers or the dispatcher of the goods. These parties are best placed to prevent hazardous substances in freight containers.

Annex 1: Example measurement report
Annex 2: Explanatory comments on the analysis and assessment

This code of practice was drawn up in conjunction with the ZfAM (the central institute of occupational medicine and maritime medicine in Hamburg).

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Annex 1: **Example measurement report**

Measurement institute:
Date:

Commissioned by:

Measurement report for screening for hazardous substances in the air within import freight containers

Date of sampling:

Container number:

Authorized agent:

Seal numbers/first and further openings:

Information on fumigation:

Location of the container at the time of sampling:

Content of the container:

Reason for measurement:

Sampling conditions: *(inside temperature, outside temperature*)

Description of the sampling and analysis methods:
(also state analysis method in the Table on Page 3)

Assessment:
(consideration of the aggregate indices, recommendations for ventilation and for measures to be taken during unloading, information on post-manufacture emissions, instructions for future selective measurements, for example definition of the range of substances)

Annex 1: **Example measurement report**

Hazardous substances with workplace exposure limits	CAS No.	Carcinogenic	Explanatory comments on the reference value	Vapour pressure 20 °C [mbar]	Analyses Methods	German workplace exposure limit [ml/m³] [ppm]	**Measued value** [ppm]	**Index I=concentration/exposure limit**
Trichloronitromethane; chloropicrin	76-06-2		German workplace exposure limit	22.5		0.1		
1,2-dichloroethylene; cis-, trans-	540-59-0		German workplace exposure limit	220		200		
Dichloromethane	75-09-2	K3A (DFG)	German workplace exposure limit	192		75		
Ethylbenzene	100-41-4	K3A (DFG)	German workplace exposure limit	10		100		
Carbon disulphide	75-15-0		German workplace exposure limit (DFG MAK value 2008: 5 ppm)	395		10		
Toluene	108-88-3		German workplace exposure limit	29		50		
Trimethylbenzene, all isomers	25551-13-7		German workplace exposure limit	Approx. 2		20		
Xylene, all isomers	1330-20-7		German workplace exposure limit	7-8		100		
Phosphine	7803-51-2		German workplace exposure limit (value for release in accordance with TRGS 512: 0.01 ppm)	35 000		0.1		
Sulphuryl difluoride	2699-79-8		German exposure limit (value for release to TRGS 512: 1 ppm)	15 500		2.39		
Aggregate index of the substances with German workplace exposure limit	-	-	-		-	-	-	

Annex 1: **Example measurement report**

Carcinogenic substances Category 1 and Category 2	CAS No.	Carcinogenic	Explanatory comments on the reference value	Vapour pressure 20 °C [mbar]	Analyses Methods	Intervention value [ppm]	**Measured value** [ppm]	**Index I=concentration/exposure limit**
Benzene	71-43-2	**C1**, M2 (GHS 1272/2008 Annex. VI Part 3.2) K1, M 3A (DFG)	No German workplace exposure limit available, since carcinogenic	100		0.1		
Trichloroethylene	79-01-6	**C2**, M3 (GHS 1272/2008 Annex. VI Part 3.2) K1, M 3B (DFG)	No German workplace exposure limit available, since carcinogenic	77		1		
1,2-dichloroethane	107-06-2	**C2** (GHS 1272/2008 Annex. VI Part 3.2)	No German workplace exposure limit available, since carcinogenic	87		0.02		
1,3-dichloropropene, isomers	542-75-6	**K2** (TRGS 905)	No German workplace exposure limit available, since carcinogenic	37		0.01		
Aggregate index of the Category 1 and Category 2 substances	-	-	-		-	-	-	

Annex 1: **Example measurement report**

Hazardous substances suspected of being potentially carcinogenic Category 3	CAS No.	Carcinogenic	Explanatory comments on the reference value	Vapour pressure 20 °C [mbar]	Analyses Methods	Orientation value [ppm]	**Measured value** [ppm]	**Index I = concentration/ exposure limit**
Formaldehyde *)	50-00-0	C3 (GHS 1272/2008 Annex. VI Part 3.2) K4 (DFG)	DFG MAK value, DFG: K4, M5, no German limit value available, since K3	2		0,3		
1,2-dichloropropane	78-87-5	K 3B (DFG)	No German workplace exposure limit available, since K3	51		75		
Bromomethane	74-83-9	K 3B (DFG)	Value for release to TRGS 512; no German workplace exposure limit available, since K3	1 900		0,5		
Methyl iodide	74-88-4	C3 (GHS 1272/2008 Annex. VI Part 3.2) K2 (DFG)	No German workplace exposure limit available, since K3	441		0,3		
Aggregate index of the Category 3 substances	-	-	-	-	-	-	-	

*) Formaldehyde need be measured only in containers carrying wood products and textiles.

Annex 2: **Explanatory comments on the analysis and assessment**

Requirements concerning analysis

Indicate your analysis method in the "Analysis method" column of the table.

- Validated analysis method involving GC/MS with multi-point calibration, ideally with certified standard TO14 multi-component mixtures (Scott from Supelco/sigma Aldrich/Restek).
- The analysis method must distinguish the above substances clearly from each other. In addition, all substances detected as relevant in the chromatogram must be stated. The chromatograms shall be presented upon request.
- Requirements concerning the limit of detection: for carcinogenic substances, as low as possible; for substances subject to a German workplace exposure limit, at least 1% of the workplace exposure limit.
- Should it not be possible to determine a substance by means of the analysis method, the task must be formulated as follows: lower than the **value** of the LOD lower level of detection, LOD = $\gamma_B + 3^* \sigma_B$, e.g. "< 0.2 ppm".
- The total of the range of substances (see above) must always be stated. Where substances have not been measured, "not measured" must be stated in the table. The statement "n.n." is not permissible, as it has led to misunderstandings.
- Formaldehyde cannot be measured by means of GC/MS; it should therefore be measured at least by detector tubes, and preferably by means of a validated HPLC method or similar.
- Procedures consistent with DIN EN 482, "Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents", and DIN EN 689, "Workplace atmospheres – Guidance for the assessment of exposure by inhalation to chemical agents for comparison with limit values and measurement strategy".

  The assessment index I = measured value/"limit value" must be stated to at least two decimal places. For smaller values, the statement I < 0.01 is sufficient.

Categories of carcinogenic substances

Carcinogenic substances or suspected carcinogens are classified in TRGS 905 and in the GHS Regulation 1272/2008 Annex VI Part 3.2. Some of the substances are not covered by these regulations; recourse is then made in addition to the classification of the MAK Commission of the DFG (German Research Foundation). The definitions differ and are therefore listed below. The categories are abbreviated to K; K1 for example corresponds to C1 in the GHS Regulation.

- **Definition of the categories to TRGS 905 and directive 67/548/EEC Annex VI**

Category 1: Substances known to be carcinogenic to man. There is sufficient evidence to establish a causal association between human exposure to a substance and the development of cancer.

Category 2: Substances which should be regarded as if they are carcinogenic to man. There is sufficient evidence to provide a strong presumption that human exposure to a substance may result in the development of cancer. This assumption is generally based upon appropriate long-term animal studies and other relevant information.

Category 3: Substances which cause concern for man owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment. There is some evidence from appropriate animal studies, but this is insufficient to place the substance in Category 2.

- **Definition of the categories – MAK Commission of the DFG**
  Category 1: Substances that cause cancer in man
  Category 2: Substances that are to be regarded as causing cancer in man, since sufficient results from long-term animal studies or evidence from animal studies and epidemiological investigations gives rise to the assumption that they make a significant contribution to the cancer risk. ….
  Category 3: Substances which, owing to known or possible carcinogenic effects, give grounds for concern, but which cannot be conclusively evaluated owing to insufficient information. …
  Category 3 A Substances which would satisfy the conditions for assignment to Categories 4 or 5; adequate information for these substances from which a MAK or BAT value could be derived does not however exist.
  Category 3 B: Evidence of a carcinogenic effect exists from in-vitro or animal studies but is not sufficient for assignment to a different category.
  Category 4: Substances with a carcinogenic effect whose dominant mechanism of action is non-genotoxic and for which genotoxic effects are of minor significance if any, provided the MAK and BAT values are observed.
  Category 5: Substances with a carcinogenic or genotoxic effect the strength of which is however deemed to be so low that provided the MAK value is observed, no significant contribution to the cancer risk in humans need be anticipated. ….

Workplace exposure limit

The workplace exposure limits are defined in the German Dangerous Chemicals Regulation and listed in the TRGS 900 technical rules.

Intervention values for Category 1 and Category 2 carcinogenic substances

By definition, occupational exposure limits do not exist for carcinogenic substances of Categories 1 and 2. The former TRGS 900 set out TRK values (technical exposure limits). The TRK value was intended to indicate the concentration of a substance which was attainable in the workplace atmosphere in accordance with the state of the art. Since 1 January 2005, the Dangerous Chemicals Regulation has embodied a new concept for limit values. Since that date, the Dangerous Chemicals Regulation has defined only health-base limit values, the workplace exposure limits. The TRK values are thus no longer valid.

In order to permit assessment of the health risk presented by carcinogenic substances in the container air and to define the point beyond which measures are necessary, "intervention values" are instead defined, based upon risk assessments found in the literature [1], [2]. These intervention values take account of typical work situations associated with the unloading of containers, and cannot be applied as limit values for other work situations.

In June 2008, the German Federal Ministry of Labour and Social Affairs (BMAS) published Announcement 910, "Risk figures and exposure-risk relationships in activities involving carcinogenic hazardous substances", but did not specify values for the substances in questino. As soon as concentration values are published by the BMAS, the hazardous substance screening concept will be adapted to the new arrangements.

[1] T. Eikmann et al. (eds.); Gefährdungsabschätzung von Umweltschadstoffen. Ergänzbares Handbuch toxikologischer Basisdaten und ihre Bewertung; Berlin 1999 – 2001, 2/2005 Kennzahl D125

[2] BIA-Handbuch, Section 120120 "Krebsrisikozahlen", issue 12/2002

Orientation values for substances suspected of being potentially carcinogenic, K3

In contrast to the "intervention values" for Category 1 and 2 substances, the measured values **must** be **as far as possible** below the stated orientation values for suspected carcinogens, since a carcinogenic effect cannot be ruled out at these concentrations, but a risk-related assessment is at the same time not possible.

- For formaldehyde, for example, a MAK value of 0.3 ppm from the DFG still exists.
- For bromomethane, the value for release stated in the TRGS 512 is applied: 0.5 ppm.
- For 1,2-dichloropropane, the foreign limit value (USA, Belgium, Canada, Denmark, France, etc.) of 75 ppm is applied.
- For methyl iodide, international limit values of 0.3 to 5 ppm exist. In the interests of safety, the lowest value of 0.3 ppm is specified.

Aggregate index

The assessment index I must be calculated for each substance. The assessment index is the quotient of the measured value C and the reference value for the exposure limit (EL: limit value, orientation value or intervention value).
The sum is then to be formed from it for assessment of the total exposure to all substances.

I = concentration/exposure limit
$I = C_1/EL_1 + C_2/EL_2 + C_3/EL_3 + C_4/EL_4 + \ldots\ldots$

I $\geq$ 1 means that measures are necessary.