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Practical guidelines

Chemical agents directive
98/24/EC

Practical guidelines – Chemical agents directive — 98/24/EC

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PRACTICAL GUIDELINES

OF A NON-BINDING NATURE ON THE PROTECTION OF THE HEALTH AND SAFETY OF WORKERS FROM THE RISKS RELATED TO CHEMICAL AGENTS AT WORK

(Articles 3, 4, 5 and 6, and Annex II, section 1, of Directive 98/24/EC)

CONTENTS

INTRODUCTION

1. PURPOSE AND SCOPE OF THE PRACTICAL GUIDELINES

Directive 98/24/EC *on the protection of the health and safety of workers from the risks related to chemical agents at work* has, as its legal basis, Article 137 of the Treaty on European Union. Accordingly, it establishes minimum health and safety conditions which must be applied by Member States, without prejudice to any stricter legislation which they may have in this respect.

This document satisfies the requirement in Article 12(2) of Directive 98/24/EC for the preparation of practical guidelines by the European Commission based on Articles 3, 4, 5 and 6, and Annex II, section 1.3, of the same Directive. It should therefore be noted that this document does not cover the whole text of the Directive, but only the aspects contained in said articles, which are:

- methods for the measurement and evaluation of workplace air concentrations in relation to the occupational exposure limit values in Directive 2000/39/EC
- risk assessment
- general principles for prevention
- specific protection and prevention measures
- surveillance of the health of workers exposed to lead and its ionic compounds

The purpose of these Practical Guidelines is to assist Member States in drawing up their national policies and to facilitate compliance with their regulations on the protection of the health and safety of workers. Despite the fact that these Practical Guidelines are for guidance only and are not binding, they shall be taken into account by Member States as far as possible, in accordance with Article 12(2) of the Directive.

This document sets out the broad outlines of preventive action with regard to chemical agents and provides some practical tools for complying with specific aspects, such as risk assessment. These tools should be regarded as an aid to Member States in ensuring correct compliance with their national regulations, especially by small and medium-sized enterprises, but not, under any circumstances, as the only tools available for this purpose.

Finally, it must be noted that there are practical problems in identifying the hazards posed by chemical agents and in assessing the risks arising from these. This is true in the following cases:

- Substances not classified as hazardous (due to their non-hazardous nature or to insufficient information being available, especially on long-term effects, which leads to these being regarded as non-hazardous until further data is available).
- Substances with insufficient information for their correct classification according to Directive 67/548/EEC, which could lead to the hazards posed by these being undervalued or overvalued, with the subsequent loss of efficacy of the classification system.
- Preparations classified according to Directive 1999/45/EC for which the assessment of their hazardous properties may not be as strict as the assessment of the properties of each of the constituent substances.

The problems resulting from these cases are not exhaustively covered in this document which is why Member States are advised to draw up more detailed guidelines in this respect.

2. DEFINITIONS

To correctly interpret these Practical Guidelines, relevant comments on the definitions contained in Article 2 of Directive 98/24/EC are offered.

> A *chemical agent* means any chemical element or compound, on its own or admixed, as it occurs in the natural state or as produced, used or released, including release as waste, by any work activity, whether or not produced intentionally and whether or not placed on the market.

It is often believed that the use of chemical agents, and therefore the risks associated with these, is restricted to the chemical and related industries, such as pharmaceuticals or petroleum, which are the ones effectively manufacturing chemical agents. This belief is wholly incorrect as these days the use of chemical agents is virtually universal, not only at work, but also (outside the scope of Directive 98/24/EC) in domestic, educational and recreational activities, in the form of cleaning products, adhesives, cosmetics, etc. As a result, the risks arising from the use of chemical agents may be present in many jobs, in industry just as in agriculture or services.

Activities which, without being specifically "chemical", have seen a large increase in the use of chemical agents in the last few years include the following:

- Construction and associated activities (carpentry, painting, water, gas and electrical installations, etc.).
- Professional cleaning, especially in industrial and some service environments where the quality of cleaning is critical, such as hospitals.
- Hospitals, where a wide variety of chemical agents is used as anaesthetics, sterilants, cytostatic agents, etc.
- Waste processing industry, where the waste itself very often is, or may contain, chemical agents and where the latter are also deliberately included in the process in order to achieve the desired results.
- Agriculture, especially intensive agriculture, where the combination of the use of enclosed or semi-enclosed cultivation units (glasshouses) and the mass use of chemical agents of various types, especially pesticides, is prevalent.

Finally, we would mention a *non-exhaustive* list of "non-chemical" activities in which chemical agents are very frequently used:

- Metalworking and mechanical industries
- Mechanical workshops
- Printing works
- Chemist's shops
- Laboratories
- Restoration of works of art
- Hairdressing salons
-

A hazardous chemical agent (HCA) is:

i) any chemical agent which meets the criteria for classification as a dangerous substance according to the criteria in Annex VI to Directive 67/548/EEC, whether or not that substance is classified under that Directive, other than those substances which only meet the criteria for classification as dangerous for the environment;

ii) any chemical agent which meets the criteria for classification as a dangerous preparation within the meaning of Directive 88/379/EEC*, whether or not that preparation is classified under that Directive, other than those preparations which only meet the criteria for classification as dangerous for the environment;

iii) any chemical agent which, whilst not meeting the criteria for classification as dangerous in accordance with (i) and (ii), may, because of its physico-chemical, chemical or toxicological properties and the way it is used or is present in the workplace, present a risk to the safety and health of workers, including any chemical agent assigned an occupational exposure limit value under Article 3.

**Replaced by Directive 1999/45/EC*

It should be noted that it is not only the toxicological or physico-chemical properties of chemical agents which lead to these being regarded as dangerous under this Directive. In fact, the temperature or pressure of the agent, its capacity to displace oxygen or the physical manner in which it is used or handled constitute hazardous characteristics under (iii).

Accordingly, water vapour can pose a risk if it is, for example, at 150ºC, just like an inert solid in the form of breathable powder. (Some Member States have occupational exposure limit values for this case, such as *unclassified particles in another form*).

Hazard is the intrinsic capacity of a chemical agent to cause harm.

According to this and the above definitions, both the intrinsic properties of chemical agents (physico-chemical and toxicological) and the way they are used or are present in the workplace constitute the hazard of chemical agents which have the potential to cause harm.

Risk is the likelihood that the potential for harm will be attained under the conditions of use and/or exposure.

A risk assessment therefore involves two variables: the harm and the likelihood that this will be attained. The intrinsic hazard posed by the agent and also the conditions of its use and handling, including the existing prevention and protection measures, must therefore be determined.

Accordingly, we can say that the presence of sulphuric acid in an undertaking will always pose a hazard. However, the level of risk may be virtually non-existent if the sulphuric acid is packaged in watertight safety containers, if the process is enclosed, etc.

The present document uses other concepts not defined in Directive 98/24/EC. The following terms are defined below according to the context in which they are used in these Practical Guidelines.

Exposure to chemical agents: is any work situation in which a chemical agent is present and the worker comes into contact with this agent, normally through the skin or via inhalation.

Accident involving chemical agents: is an abnormal event occurring rapidly and unexpectedly during work and which results in workers being suddenly exposed to chemical agents or the energy released by these.

3. MECHANISMS GENERATING THE HARM CAUSED BY CHEMICAL AGENTS

Chemical agents can cause harm to the human body either *directly* or by *producing some form of energy* which can have an adverse effect on human health.

In the *first case*, for a chemical agent to harm the human body directly, it is necessary (but not sufficient) for its molecules to come into contact with some part of the body.

The harm may become apparent rapidly or even immediately after contact (*acute effect*) or may appear in the long term, normally due to repeated exposure over time (*chronic effect*).

In addition, the harm may become apparent at the point of contact between the chemical agent and the body (skin, respiratory system, gastrointestinal tract), in which case this is termed a *local effect*, or it may appear, following a process of absorption and distribution through the body, at any point of the body regardless of the place where the contact occurred (*systemic effects*). Examples of local effects would be the respiratory irritation produced by inhaling ammonia or the burning of the skin produced by contact with sulphuric acid. Examples of systemic effects are the hepatic damage caused by inhaling certain solvents or the neurological damage caused by inhaling mercury vapours.

In the *second* case mentioned, the harm is caused by the energy produced by the fire or explosion of chemical agents capable of giving rise to this type of phenomenon.

Fires in the workplace can cause serious harm to workers, especially if appropriate emergency measures have not been adopted, and almost always result in major damage to the undertaking's assets.

Explosions occur when a sudden oxidation or decomposition reaction occurs, producing a temperature or pressure rise, or both simultaneously. Due to their virtually instantaneous nature, explosions usually have very severe effects on both persons and material assets.

Due to the destructive potential of explosions, the European Union has published Directive 94/9/EC on equipment and protective systems intended for use in potentially explosive atmospheres and Directive 1999/92/EC (ATEX) on work in explosive atmospheres. The latter has resulted in the publication of a Guide of Good Practice by the European Commission.

4. STRUCTURE OF THE GUIDE AND REFERENCE TO DIRECTIVE 98/24/EC

Table 1 sets out the correspondence between the contents of the Guide and the provisions of Directive 98/24/EC.

Table 1 Contents of this Guide and their correspondence with Directive 98/24/EC

PART	CHAPTER	TITLE	Reference in Directive 98/24/EC
Part I		Identification, assessment and control of risks	
	1.	Identification and assessment of risks arising from the presence of hazardous chemical agents	Article 4
	2.	Principles for prevention to eliminate or minimise risks	Article 5(2)
	3.	Specific protection and prevention measures to control risks	Article 6(2)
Part II		Biological monitoring and surveillance of the health of workers exposed to lead and its ionic compounds	Section1.3 Annex II
Part III		Bibliography	
ANNEXES			
	Annex 1	Risk (R) and Safety (S) phrases and their combinations	
	Annex 2	Simplified risk assessment methods	
	Annex 3	Application examples of the principles for prevention and specific measures in two industrial processes	
	Annex 4	Quantitative evaluation of exposure to chemical agents	
	Annex 5	Standardised methods for the measurement of workplace air concentrations of hazardous chemical agents in relation to the occupational exposure limit values	Article 3(10)
	Annex 6	Analytical method sheets for lead and its ionic compounds in air and blood	

5. LEGISLATION SUPPLEMENTING DIRECTIVE 98/24/EC

A *non-exhaustive* list of provisions supplementing Directive 98/24/EC which apply within the European Union is provided below. These can be grouped into the following areas:

a) Identification of HCAs

- Council Directive 67/548/EEC, as amended and adapted to technical progress, on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances.

- Directive 1999/45/EC of the European Parliament and of the Council, as subsequently adapted to technical progress, relating to the classification, packaging and labelling of dangerous preparations.

- Commission Directive 91/155/EEC, as amended, by Directive 2001/58/EC defining and laying down the detailed arrangements for the system of specific information relating to dangerous preparations and substances (Safety Data Sheets).

b) Chemical safety

- Council Directive 96/82/EC on the control of major-accident hazards involving dangerous substances. Subsequent Commission decisions on its application.

- Directive 94/9/EC of the European Parliament and the Council on the approximation of the laws of the Member States concerning equipment and protective systems intended for use in potentially explosive atmospheres.

- Directive 1999/92/EC on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres.

c) Work with particular HCAs

- Directive 2003/18/EC of the European Parliament and of the Council amending Council Directive 83/477/EEC on the protection of workers from the risks related to exposure to asbestos at work.

- Council Directive 90/394/EEC, as amended (Directive 97/42/EC and Directive 1999/38/EC), on the protection of workers from the risks related to exposure to carcinogens at work.

d) Transport of dangerous goods (DGs)

- Technical Instructions for the Safe Transport of Dangerous Goods by Air (ICAO[1]).

- International Maritime Dangerous Goods (IMDG[2]) Code.

- Carriage of Dangerous Goods by Inland Waterways (ADN[3]).

- 97/C 267/96. Proposal for a Council Directive on the approximation of the laws of the Member States with regard to the transport of dangerous goods by vessels on inland waterways, as subsequently amended.

[1] International Civil Aviation Organisation.
[2] International Maritime Dangerous Goods Code.
[3] European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways.

- European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR[4]).

- Regulations concerning the Carriage of Dangerous Goods by Rail (RID[5]).

Clearly, the specific characteristics of particularly sensitive workers must also be taken into account in applying Directive 98/24/EC, in particular through Directives 94/33/EC on the protection of young people at work and Directive 92/85/EEC on the introduction of measures to encourage improvements in the safety and health at work of pregnant workers and workers who have recently given birth or are breastfeeding.

Part III of this document, containing the Bibliography, indicates other Directives and Regulations supplementing Directive 98/24/EC.

[4] European Agreement concerning the International Carriage of Dangerous Goods by Road.
[5] Regulations concerning the International Carriage of Dangerous Goods by Rail.

PART I

IDENTIFICATION, ASSESSMENT AND CONTROL OF RISKS ARISING FROM THE PRESENCE OF HAZARDOUS CHEMICAL AGENTS IN THE WORKPLACE

1. IDENTIFICATION AND ASSESSMENT OF RISKs arising FROM THE PRESENCE OF CHEMICAL AGENTS IN THE WORKPLACE

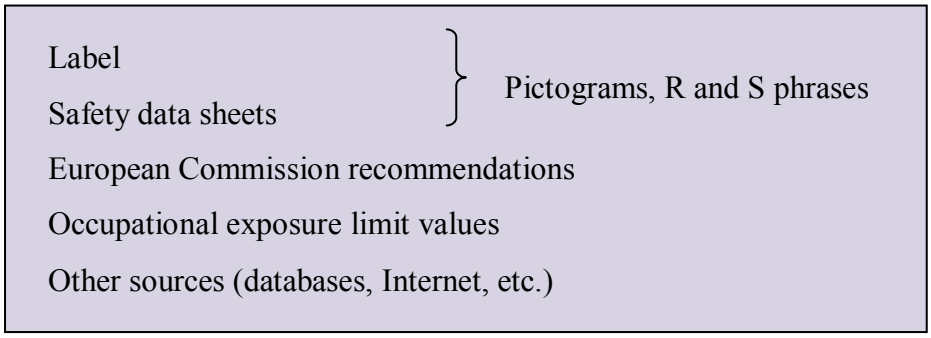
1.1 SOURCES OF INFORMATION ON THE HAZARD POSED BY CHEMICAL AGENTS

Chemical agents present in the workplace may pose risks to the health or safety of workers on account of:

- their hazardous properties (physico-chemical or toxicological) (e.g.: explosive or sensitiser)
- the temperature or pressure at which they occur in the workplace (e.g.: water vapour at 150ºC)
- their capacity to displace the atmospheric oxygen from the workplace (e.g.: pressurised inert gas)
- the manner in which they are present in the workplace (e.g.: inert solid in the form of a breathable powder)

To determine the capacity of chemical agents present in the workplace to pose risks, the hazardous properties of these agents and the way in which they are used or are present must therefore be known. Information on the hazardous properties of chemical agents present in the workplace, which is the first step in assessing these risks, can be obtained from the sources indicated below:

Information on the hazard posed by chemical agents



1.1.1 Label

In accordance with the legislation resulting from the European directives on the classification, packaging, labelling and system of specific information relating to substances and preparations (which we will refer to as chemicals), all containers of hazardous chemicals placed on the market must be labelled according to a defined model. Only if the product is delivered in bulk is such a label not required (however, if the product has been transported, there will be a specific label for the transport).

The contents of the label (see Figure I.1) provide information on the following points:

a) Identification of the chemical.
b) Identification of the manufacturer or supplier.
c) Intrinsic hazard posed by the product due to its properties or effects. This includes the following data:
   - Classification of the product in accordance with defined hazard categories. This classification is shown by a combination of hazard indications and symbols in accordance with the correspondence indicated in Table I.1. These symbols readily draw attention to the general hazardous properties of the product.
   - R risk phrases assigned to the product from the list indicated in Annex 1. These phrases describe the specific effects of a product on human health or the environment or the hazardous properties affecting safety. They constitute basic information which must be borne in mind when assessing risks.
   - S safety phrases assigned to the product from the list indicated in Annex 1. These constitute safety advice which must be borne in mind when handling and using the product.

The information included on the label can also be found in the safety data sheets where it is expanded and supplemented by other data of interest.

Figure I.1 Labelling of chemicals

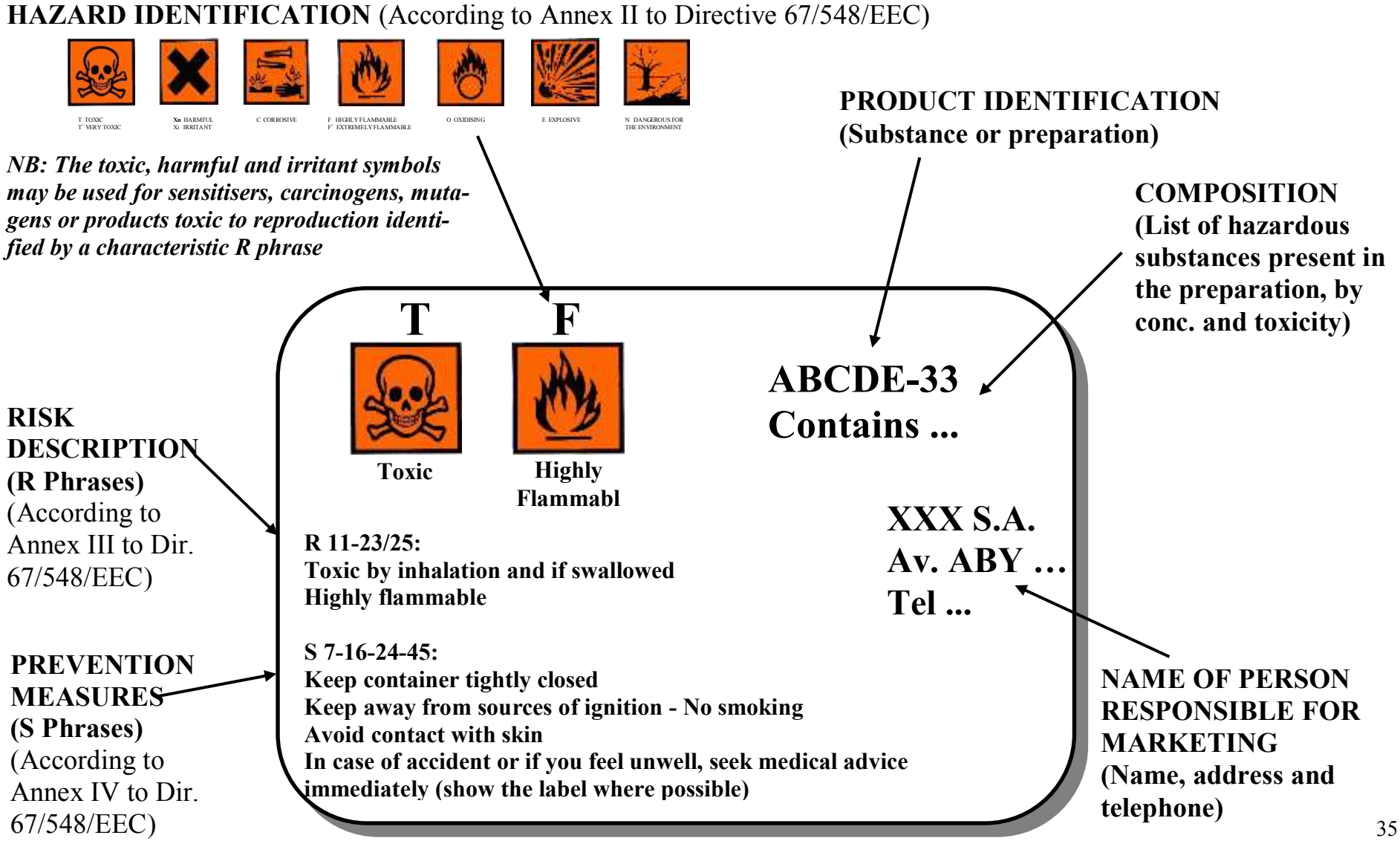


Table I.1 **Hazard classification, symbols and indications**

Properties or effects	Hazard categories	Identification	
Physico-chemical	Explosive		
	Oxidising		
	Extremely flammable		
	Highly flammable		
	Flammable	R10	
Toxicological	Very toxic		
	Toxic		
	Harmful		
	Corrosive		
	Irritant		
	Sensitising	By inhalation	R42 

Properties or effects	Hazard categories		Identification
Specific effects on health	Carcinogenic	Cat. 1 and 2	R45 or R49 
		Cat. 3	R40 
	Mutagenic	Cat. 1 and 2	R46 
		Cat. 3	R68 
	Toxic to reproduction	Cat. 1 and 2	R60, R61 
		Cat. 3	**R62, R63** 
Effects on the environment	Dangerous for the environment		**R52, R53, R59*** 

** The R phrases or the pictogram may be used in this case*

		By skin contact	R43 

1.1.2 Safety data sheets

The Safety Data Sheet (SDS) supplements the label, by offering information which may not already be contained therein.

Also in accordance with the legislation indicated above, suppliers of hazardous chemical agents, whether packaged or in bulk, must provide professional users with an SDS relating to the product supplied. In addition to this, suppliers of preparations must provide a safety data sheet at the request of professional users if the preparation is not classified as hazardous but contains an individual concentration ≥ 1% by weight, in the case of non-gaseous preparations, and ≥ 0.2% by volume, in the case of gaseous preparations, of at least one substance which is dangerous to health or the environment, or a substance for which there are Community exposure limits in the workplace.

The purpose of the SDS is to provide professional users with effective and adequate information about the hazard posed by the product to health, safety and the environment, to enable them to assess the possible risks posed by the use of these agents to workers, and to assess the hazard posed by other agents if their substitution is proposed.
These sheets must be written in the language of the country to which the supply is made and must be dated. The contents of the sheets must be updated when new data becomes available and changes must be notified to recipients.

The extensive information included in safety data sheets must be grouped into the following 16 sections, in accordance with the model specified in Directive 91/155/EEC as amended by Directive 2001/58/EC:

1. Identification of substance/preparation and company/undertaking.
2. Composition/information on ingredients.
3. Hazards identification.
4. First-aid measures.
5. Fire-fighting measures.
6. Accidental spillage measures.
7. Handling and storage.
8. Exposure controls/personal protection.
9. Physical and chemical properties.
10. Stability and reactivity.
11. Toxicological information.
12. Ecological information.
13. Disposal considerations.
14. Transport information.
15. Regulatory information.
16. Other information.

In line with its purpose, all the information included in an SDS is essential for an effective analysis of the hazards associated with a particular product. For this reason the SDS is the basic source of information for assessing the risks posed by the presence of chemical agents in the workplace. Table I.2 shows how the data contained in the various sections of the sheet are laid out.

The importance of safety data sheets justifies undertakings setting up a specific management procedure to ensure that their use is optimised.

Table I.3 summarises the various actions which may be included in an appropriate procedure for managing SDSs. These actions have a number of purposes:

- To establish and maintain an up-to-date register of the SDSs corresponding to the various chemicals used within the undertaking, and to this end maintaining necessary contacts with suppliers, so as to be able to obtain necessary information on products for which SDSs are not available.

- To compare the information contained in SDSs with the labels of chemicals and the conditions under which these are used in the undertaking; this shall always occur when the SDS is new or a new version.

- To use the information contained in SDSs when assessing risks in the workplace and also in the actions which it is decided to take in relation to:
    - Worker training
    - Safety instructions
    - Worker information
    - Emergency procedures (including information useful for external emergency services)

- To make the SDSs available to occupational medicine services for use in connection with risk assessments and health surveillance and with possible advice on emergency procedures.

- To always keep SDSs available for consultation by workers or their representatives.

Table I.2* Application of Safety Data Sheets

General information	**Section**
- Name of manufacturer and supplier	**1**
- Chemical composition	2
- Physico-chemical properties	9

Use	**Section**
- Recommended uses and restrictions	**16**
- Handling and storage	**7 and 15**
- User protection	**8**
- Exposure limit value	**8 and 15**
- Restrictions on marketing and use	**15**

Transport	**Section**
- Precautions and advice	**14**
- Hazards posed during transport	14

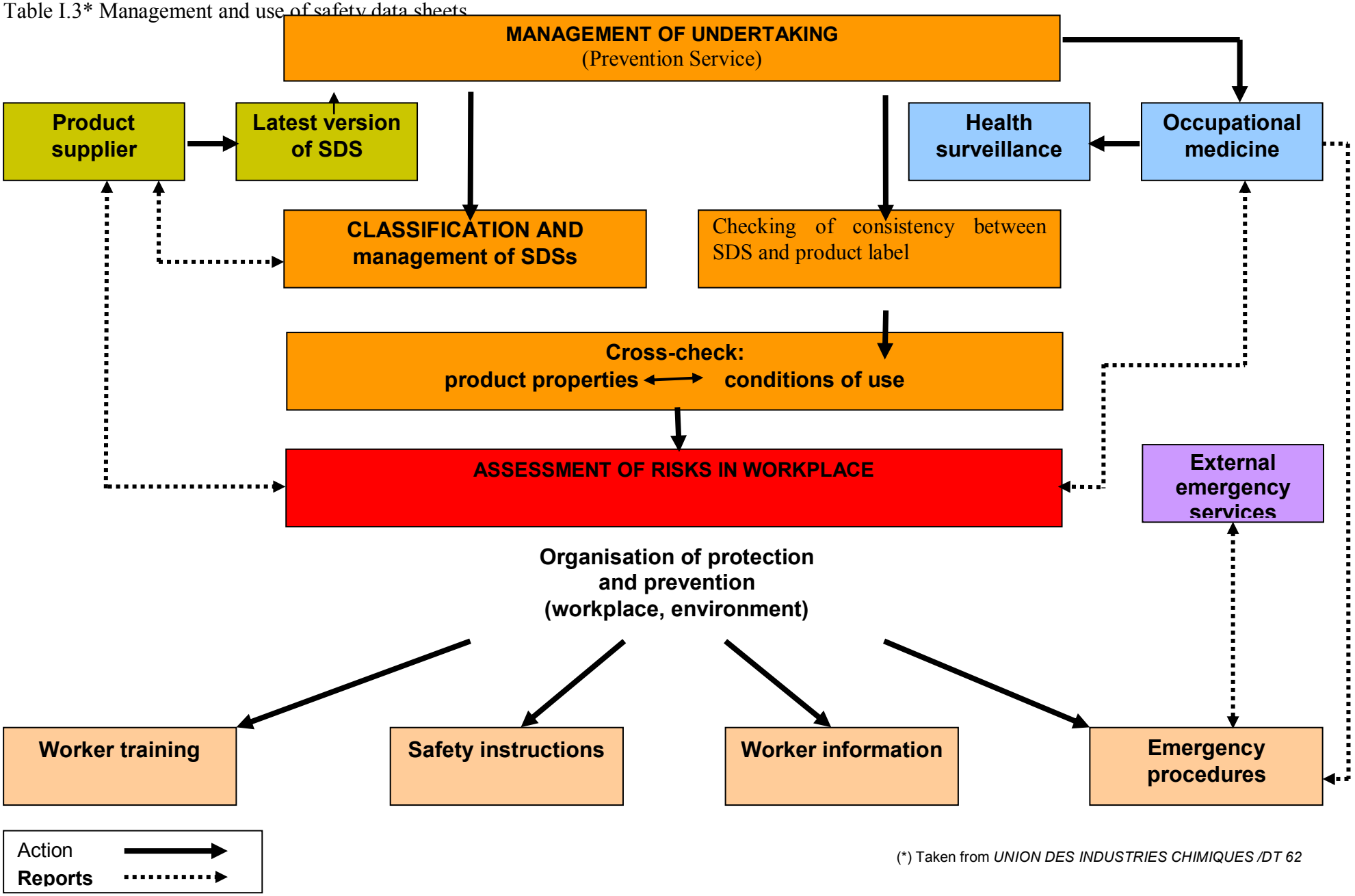
Hazards	**Section**
- Safety: Flammability, explosiveness, reactivity	**3, 9 and 10**
- Health: toxicity	**3 and 11**
- Environment: ecotoxicity	**3 and 12**

Disposal	**Section**
- Waste, recycling	**13**

Emergencies	**Section**
- First aid	**4**
- Fire	**5**
- Leaks / releases	**6**

(*) Taken from *UNION DES INDUSTRIES CHIMIQUES /DT 62*

Table I.3* Management and use of safety data sheets



(*) Taken from *UNION DES INDUSTRIES CHIMIQUES /DT 62*

1.1.3 Occupational exposure limit values and biological limit values

Occupational exposure limit values and biological limit values are specific reference parameters used in assessing risks due to exposure to chemical agents in the workplace.

Limit values may be of two types, depending on whether they have been established solely taking into account health criteria or whether they also take account of viability criteria. In the first case, they form references to ensure the health of workers. In the second case, which includes limits of genotoxic agents (carcinogens or mutagens), they form references for the level of risk which must not be exceeded at any time. Lists of limit values must clearly distinguish between the two types of value.

All EU Member States must have their own national list of exposure limits and biological limits in accordance with Directive 98/24/EC. The limit values which are to be used for risk assessments in each country are those indicated in said list, applied according to their nature.

It should not be forgotten that, according to Community legislation (Directive 98/24/EC), any substance which has an exposure limit value must be regarded as a hazardous substance. This is the case with particles of insoluble materials which are not classifiable as dangerous to health. The same applies with substances produced by decomposition or in the heat treatment of certain materials, such as certain plastics, some metals (welding and other applications), coal tar, etc.

1.1.4 European Commission recommendations on the results of risk assessments and the risk limitation strategy for substances.

These are recommendations made in accordance with Council Regulation (EEC) No 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances. They relate to 141 substances which were selected as as priorities for evaluation. The evaluation included an assessment of the risks to workers and contains valuable information for carrying out risk assessments under 98/24/EC.

These recommendations were published in the Official Journal of the European Communities, L series. Some of the risk reduction strategies make reference to use of this guidance and to other worker related measures. The assessments are available at:: http://ccb.jrc.it/existing-substances.

1.1.5 Other sources

If the information in the safety data sheet for a product is insufficient for a proper assessment of the risks of its presence in the workplace or, if it is an agent which is not subject to the provisions on the marketing of hazardous products, **the provision of a safety data sheet is not compulsory**, professional users may request the necessary information from producers or suppliers in accordance with the provisions of Article 8(3) of Directive 98/24/EC.

In any event, information of interest can be obtained from other sources, as indicated below:

- Existing regulations on the carriage of dangerous goods by road (ADR[6]), rail (RID[7]), air (ICAO-TI[8]) and sea (IMDG Code[9]) or river (ADN[10]). These indicate hazard classifications for chemicals and their corresponding symbols (pictograms) and indications.

[6] European Agreement concerning the International Carriage of Dangerous Goods by Road
[7] Regulations concerning the International Carriage of Dangerous Goods by Rail
[8] International Civil Aviation Organisation – Technical Instructions
[9] International Maritime Dangerous Goods Code
[10] European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways

- Monographs and data sheets for chemical substances, produced by various institutions based on existing scientific and technical information, such as the international chemical safety cards prepared under the auspices of the UN[11], ILO[12] and WHO[13], with the cooperation of the EU Commission, which among other data relevant to risk prevention include data on the toxicity of substances and permissible concentration limits.
- Databases which can be accessed on CD-ROM or on-line.
- Bibliographical databases which contain summaries of work published in specialist journals.

[11] United Nations Organisation
[12] International Labour Organisation
[13] World Health Organisation

1.2 RISK ASSESSMENT PROCEDURES

To ensure that risks to the health of persons are fully controlled, Directive 98/24/EC states that employers have a duty to determine whether any hazardous chemical agents are present at the workplace, to eliminate these and, where this is not possible, to *assess the risk* to which they may give rise.

The basic purpose of the assessment is to determine the risks in order to eliminate them. Risk elimination is actually the first principle for prevention, as provided for by Framework Directive 89/391/EEC in Article 6(2)(a) thereof. Unfortunately it is not always possible to eliminate risks which is why the assessment acts as a basis for reducing these as it allows priorities to be established, the necessary prevention measures to be determined and the efficiency of those already in existence to be discovered.

Risk assessment is fundamentally a process of information and investigation of the hazardous properties of chemical agents present and of the conditions under which people work with these, in order to determine the existing risks, the persons exposed and the possible harm which may occur (including the possible existence of individual susceptibility), with a final evaluation of the possibility of such harm being attained.

We have indicated previously that the risks of HCAs arise through both *direct contact* between the HCA and the human body and through the action which the *energy generated* when an HCA is involved in a chemical reaction such as a fire or explosion can have on the body.
It should be noted that the risks to be assessed under Directive 94/28/EC deriving from the presence of hazardous chemical agents may be one or more of the following:

- Risk of fire and/or explosion.
- Risk generated due to hazardous chemical reactions which may affect the health and safety of workers.
- Risk due to inhalation.
- Risk due to absorption through the skin.
- Risk due to contact with the skin or eyes.
- Risk due to ingestion.
- Risk due to penetration through the parenteral route.

One risk factor to be taken into account, regardless of the intrinsic hazard posed by the agent, is faults in the installations which may have consequences on the health and safety of workers. This is why the chemical risks deriving from these faults must be taken into account. Table I.1 sets out diagrammatically the possible risks due to hazardous chemical agents and also contains a non-exhaustive list of the accompanying circumstances (conditions, properties, factors, etc.).

Table I.1 Risks arising from the presence of hazardous chemical agents

Risk	Some risk factors
Risks of fire and/or explosion	• Physical state (gas, vapour, fine dust, etc.) • Pressure / Temperature • Flammability of the hazardous chemical agent • Calorific value of the materials • Environmental concentration (flammability limits) • Sources of ignition (smoking, naked flame operations, tools, footwear, static discharges, exothermic chemical reactions)
Risks due to hazardous chemical reactions	• Chemical reactivity and instability of hazardous chemical agents • Inadequate cooling systems • Unreliable system for controlling key variables in the reaction (pressure, temperature and flow control)
Risks due to inhalation of the agent	• Toxicity of the hazardous chemical agent • Environmental concentration • Exposure time • Particularly sensitive workers
Risks due to absorption through the skin	• Location and extent of the contact between the chemical agent and the skin • Toxicity of the hazardous chemical agent via the skin • Duration and frequency of contact • Particularly sensitive workers
Risks through the parenteral route	• Toxicity of the hazardous chemical agent • Damage to the skin • Particularly sensitive workers
Risks due to ingestion	• Toxicity of the hazardous chemical agent • Personal hygiene habits • Possibility of eating, drinking or smoking at the work post • Particularly sensitive workers
Risks due to contact between the skin or eyes and the chemical agent	• Incorrect use of personal protective equipment • Inappropriate work procedure • Incorrect transfer system
Chemical risks arising from installations which may have consequences on the health and safety of workers	• Corrosion of materials and installations • Non-existence of facilities for controlling leaks and spills (retaining trays, protection against mechanical impacts) • Non-existence of preventive maintenance

Furthermore, prolonged contact with the HCA (from a few minutes to years) may be necessary for the harm to health to appear, or a relatively short or even instantaneous time may be sufficient. In the former case we will talk about risk due to exposure and, in the latter, risk of an accident. Given the intrinsic differences between the two categories, the resulting risks cannot be assessed together but must be considered separately.

Risk assessment can be carried out with various levels of thoroughness. In this respect, and as an alternative to detailed and complex assessments, in some cases simplified methods of risk assessment may be used. Table I.4 shows the various options for assessing risks due to chemical agents.

Table I.4 Methods for assessing the risk due to the presence of hazardous chemical agents (HCAs) in the workplace

	Simplified assessments	**Complex assessments**
Risk due to exposure (a)	See method proposed in Annex 2.A	Environmental measurements according to EN 689:1995 (see Annexes 4 and 5)
Risk of accident (b)	See method proposed in Annex 2.B	• HAZOP[14] • Fault trees[15] • Event trees[16]

(a) *Risks due to exposure* to a hazardous chemical agent are assessed through the criteria usually used for industrial hygiene, bearing in mind the following variables:

- **The hazardous properties of the chemical agents, in particular the information contained in the safety data sheet which the supplier is obliged to provide and the occupational exposure limit values or biological limit values established by law.**
- **The type of exposure (skin, inhalation, etc.)**
- **The duration of the exposure.**
- **The working conditions with regard to said agents, including quantities of the agent.**
- **When available, conclusions drawn from health surveillance studies.**

In general, *any consideration of working conditions must include the results of environmental measurements carried out in relation to occupational exposure limit values*. When an occupational exposure limit value effectively established within a Member State is exceeded, employers must act

[14] HAZOP (Hazard and Operability) is a method consisting of a critical, formal and systematic examination of an engineering process or project in a new installation to assess the potential risk of the operation or incorrect operation of the individual components of the equipment and their effects on the installation as a whole. This method was developed by ICI (Imperial Chemical Industries) in the United Kingdom for application in the design of pesticide plants.

[15] The Fault Tree Analysis method starts with the prior selection of the "undesirable event or event to be avoided" (Top Event). The various combinations of situations which may give rise to this event are systematically represented. Each event is generated from lower level events with the connecting link between levels being the "AND" or "OR" logic gates or operators. The fault tree, using Boolean algebra, allows the "minimum set of faults" which may lead to the "undesirable event" to be determined.

[16] Event trees are an inductive method starting from an initiating event and, depending on the responses of the various safety elements incorporated in the installation, the tree describes the accidental sequences which may lead to various events.

immediately, taking into account the nature of said limit, to remedy the situation by adopting prevention and protection measures.

However, and in accordance with the provisions of Directive 98/24/EC (Article 6(4)), environmental measurements can be avoided where *"the employer clearly demonstrates by other means of evaluation that adequate prevention and protection have been achieved"*. Accordingly, simplified evaluation systems such as that described further on (Annex 2, Part A) may be used initially. This type of simplified method also has the advantage of allowing a semi-quantitative approximation of the magnitude of the risk if there is no exposure limit value.

In any event, EN 689:1995 may be used when evaluating exposure to hazardous chemicals due to inhalation. Annex 5 includes practical guidelines which are based on this standard.

(b) The assessment of risks arising from the capacity of hazardous chemical agents to cause accidents, in particular fires, explosions or other hazardous chemical reactions, covers:

- hazards resulting from the physico-chemical nature of the chemical agents,
- risk factors identified in their storage, transport and use, and
- the estimated consequences in the event of occurrence.

Complex methods such as HAZOP, Fault Trees, Event Trees, etc. exist in order to assess this type of risk. We will not consider these in detail as they are universally known and applied. These methods should be used in accordance with the following criteria:

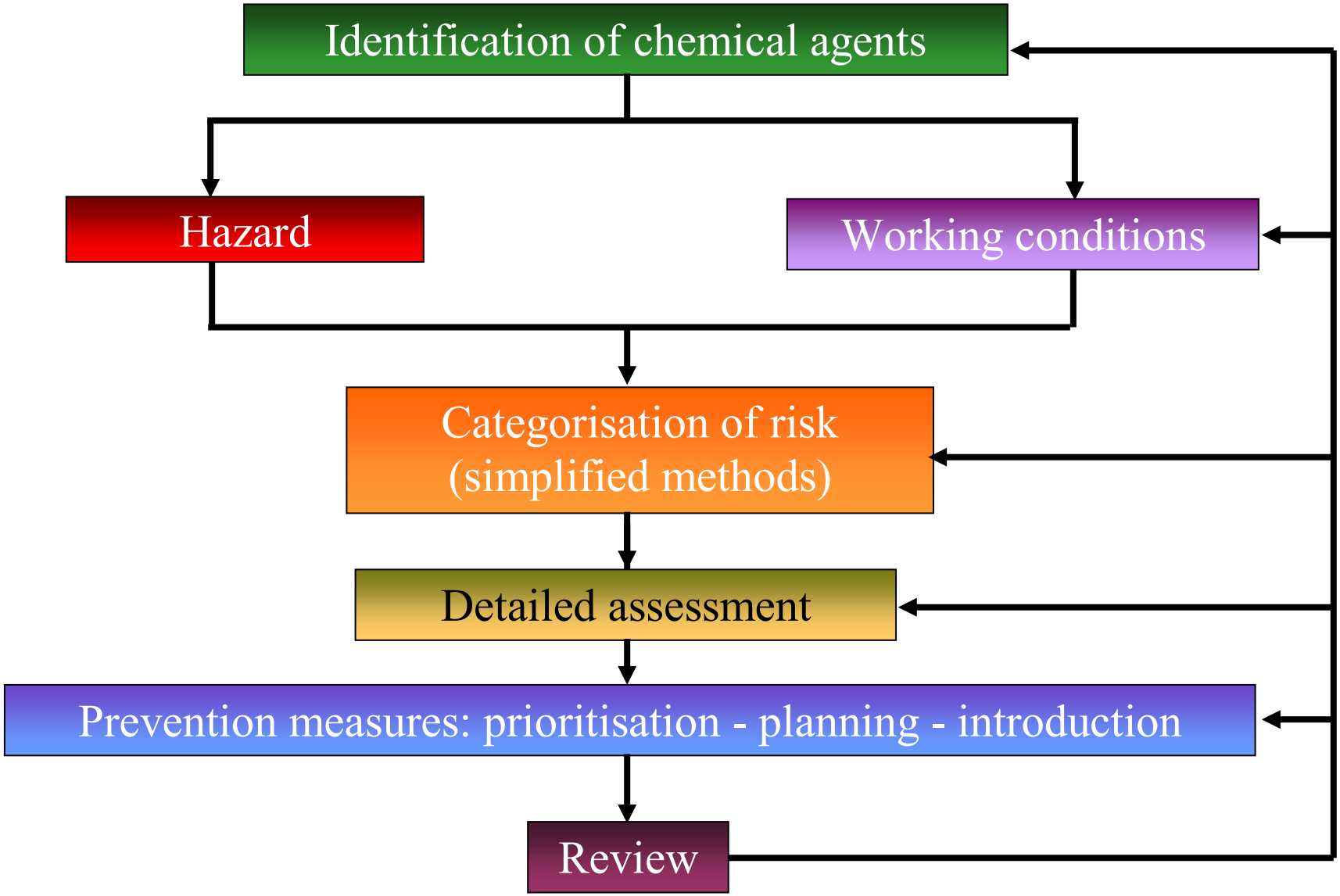
- They should be used when the consequences of the occurrence of the risk may be very serious, in terms of both human losses and material or environmental losses, within the undertaking itself or outside this.
- They require a thorough knowledge of the installations.
- Their application normally requires the involvement of a work team guaranteeing a thorough knowledge of various areas (process, instrumentation, maintenance, prevention, engineering, etc.)
- Given the severity of the possible consequences, it is normal to focus the analysis on the maximum damage to which an accident may give rise (*top event)*.

Furthermore, simplified assessments (as proposed in Annex 2, Part B) can be used when it is unreasonable to expect catastrophic consequences to result from an accident. In general, their aim is not to calculate the absolute value of the risk but, in the interests of simplicity, to provide only an approximation of the magnitude of the risk. This will often be sufficient to establish a risk hierarchy and thus determine the priorities in the preventive action.

Table I.5 shows, diagrammatically and sequentially, the various stages involved in risk prevention when working with hazardous chemical agents. These stages are all taken into account in Part I of these Practical Guidelines. Chapter 1 of Part I has provided information on identification and general aspects of risk assessment. Annex 2 to these Practical Guidelines offers two simplified methods for categorising risk (recommended step before moving on to the detailed risk assessment). The following chapters, 2 and 3, respectively develop the principles for prevention (applicable in any work situation involving hazardous chemical agents) and the prevention and protection measures (including 16 sheets describing this type of measure).

The path in the diagram is repetitive as the risk assessment and efficacy of existing prevention measures must be periodically reviewed (and always before any change in the chemical agents or working conditions).

Table I.5 **Action diagram for risk assessment and resulting actions**



2. General principles for preventing risks related to HCAs

The principles of preventive action developed in this chapter must be regarded as an extension to those set out in Article 6(1) and (2) of Directive 89/391/EEC applied to activities involving hazardous chemical agents. These principles appear in Article 5 of Directive 98/24/EC after the following paragraph:
*"*Risks to the health and safety of workers at work involving hazardous chemical agents shall be eliminated or reduced to a minimum by ...*"*

The risk due to work involving a hazardous chemical agent is eliminated when that agent disappears. It is therefore desirable to substitute this with another chemical agent or process enabling the risk to be eliminated or reduced. Where this is not technically possible, the risk must be reduced by applying prevention or protection measures. Normally, the result of the risk assessment and the information drawn from this allows the prevention measures which should be adopted to be determined.

The general principles for prevention must be applied whenever working with hazardous chemical agents regardless of whether the risk assessment also indicates a need to apply specific prevention measures. Applying these principles involves integrating the basic aspects of prevention into the work organisation and, in general, using logic and common sense in work involving hazardous chemical agents.

PRINCIPLES FOR ELIMINATING OR REDUCING RISK
• *Design and organisation of systems of work at the workplace* • *Provision of suitable equipment for work with chemical agents and maintenance procedures which ensure the health and safety of workers at work* • *Reducing to a minimum the number of workers exposed or likely to be exposed* • *Reducing to a minimum the duration and intensity of exposure* • *Appropriate hygiene measures* • *Reducing the quantity of chemical agents present at the workplace to the minimum required for the type of work concerned* • *Suitable working procedures including arrangements for the safe handling, storage and transport within the workplace of hazardous chemical agents and waste containing such chemical agents* • *Information and training of the workforce*

Design and organisation of systems of work.
Integrating prevention into the undertaking's activity involves taking this into account right from the design stage of the production processes: painting by dipping or spraying, using a high- or low-pressure chemical process or using a degreaser of one type or another, for example, must be carried out taking into account not only technological and economic aspects but also, *at the same time*, the risks which may be posed to the health of workers by each of the possible options.

Although technology often can, and in fact does, partly influence the organisation of work, this influence is usually far from absolute. There is therefore usually a wide range of organisational options in the choice of which preventive aspects must also be taken into account.

Provision of suitable equipment for work with chemical agents and maintenance procedures which ensure the health and safety of workers at work
Equipment must be chosen and installed bearing in mind the hazardous nature and characteristics of the agent to be used or produced and the environment in which this is to be installed (for example, for equipment intended for explosive atmospheres, control systems and actuators should be used which are totally pneumatic or hydraulic and, if electric, they should be explosion-proof). Selection and procurement of work equipment will be subject to the requirements of the applicable product safety directives (98/37/EC, 94/9/EC, etc.) and equipment without a CE mark and its use shall comply with the requirements of Directive 89/655/EEC.

Equipment and installations on whose suitability and proper condition the safety of the process depends must be subject to a strict schedule of servicing and maintenance which must be recorded documentarily.

Reducing to a minimum the number of workers exposed or likely to be exposed
When the risk cannot be eliminated, there is a likelihood that damage (consequences) will be attained and occur. One obvious way of lessening the consequences is for the number of persons exposed to the risk to be as small as possible. This measure, which does not reduce individual risk, does lower the overall risk involved in working with hazardous chemical agents. In practice, this is achieved by organising tasks in such a way that they are performed by the minimum number of persons needed, by segregating the work areas involving hazardous chemical agents from the rest of the undertaking's activities and by restricting access to areas where the risk exists.

Reducing to a minimum the duration and intensity of exposure
Exposure to a chemical agent by inhalation can be quantified simply by multiplying the environmental concentration by the exposure time to the agent. Reducing either of the two variables will reduce exposure. Organising work in such a way that exposure time is reduced to a minimum, by reducing this to that needed, is to be recommended.

The environmental concentration value depends on various factors, in particular the degree or level of generation of the chemical agent and the ventilation of the workplace.

The environmental concentration of a chemical agent generated during work increases continuously in unventilated premises. All workplaces (and, with all the more reason, those in which there are hazardous chemical agents) must comply with the minimum ventilation requirements laid down in Directive 89/654/EEC.

The generation of a chemical agent involves process characteristics such as temperature or pressure and the energy which is generally involved. Adjusting parameters like those mentioned to the values actually needed for the process, or simply performing certain manual operations carefully, often leads to a considerable improvement in conditions. Examples of these actions are:

- Adapting (reducing) the pressure of the supplied air used in operations involving spraying paint, solvents, sand, etc.
- Avoiding open evaporation surfaces (baths, tanks, containers).
- Adjusting the necessary temperature or electrical current density in electrolytic reactions, in open baths, to reduce evaporation and entrainment of spray (mists).
- Acting carefully in simple manual operations which can easily cause contamination (release from bags, transport of open bags or trays, cleaning of equipment by shaking or using compressed air, etc.)

Appropriate hygiene measures
Exposure to a chemical agent can occur due to contact with the skin. In general, direct contact between chemical agents and skin must be avoided and, when this accidentally occurs, the skin must be quickly washed. Impregnated clothing must also be immediately changed since it provides a contact surface and consequently gives rise to absorption through the skin. Moreover, dirty clothing can represent an additional source of contamination.

Habits which are contrary to the most basic concepts of hygiene, such as smoking, eating or drinking in workplaces, must be eradicated, with all the more reason when working with hazardous chemical agents since they foster involuntary and systematic ingestion of these agents. For reasons such as those mentioned, establishing good personal hygiene practices through actions such as the following is to be recommended:

- Prohibiting eating, drinking or smoking in areas where hazardous chemical agents may be present;
- Maintaining minimum standards of cleanliness for work clothing and its habitual use instead of street clothing.
- Availability and use of personal hygiene facilities before meals and at the end of the day.
- Washing products, such as skin care products, must under no circumstances be aggressive.
- Attention to the special needs of pregnant or breastfeeding workers.

Furthermore, extending hygiene measures to premises and installations, while ensuring that cleaning operations do not constitute an additional risk for workers, is to be recommended. Solid substances in the form of dust or fibres deposited on floors and other surfaces can return to the breathable working environment due to draughts present or generated by the passage of persons or vehicles which can in turn break these substances down into smaller particles and facilitate their dispersal through the air, thus increasing their environmental concentration.
Spillages of liquids on the floor and work machinery, and also impregnated papers and cloths, can become secondary sources for the generation of chemical agents. Therefore, workers must be encouraged to keep their work area clean and to avoid accumulating materials containing hazardous chemical agents.

The vacuum-cleaning of workplaces with a frequency reflecting the extent of the problem, which should be determined through the risk assessment, is to be recommended. Usually, daily floor cleaning, supplemented by more thorough cleaning operations extending to walls and ceilings and, in general, places which are difficult to reach, is necessary.

Spillages must be removed or cleaned up, depending on the case in question, using absorbent or neutralising agents which, once used, will be deposited in waste containers for removal and, as appropriate, subsequent treatment.

Reducing the quantity of chemical agents present at the workplace to the minimum required for the type of work concerned.
The magnitude and consequences of an explosion or a fire may depend on the quantity of a chemical agent present at the workplace. Also the risk by inhalation or contact with chemical agents is related with the quantity. In effect, even though the concentration in the air depends on the properties and conditions of the chemical agent, such as volatility and temperature, there is a relation, in general, between the concentration in the air and the quantity used in the workplace. Knowing that the quantity is a factor that determines the magnitude of the risk it is necessary to reduce it to the achievable minimum in each operation, because that leads to an efficient reduction of the intensity of the exposure. The recommended minimum quantity of a chemical agent in the workplace is not an absolute value but it depends on its hazardous properties, taking special importance, for instance, in the case of flammable, sensitising or carcinogenic substances (see table A2.4 and A2.5 in annex 2).

The use of containers of low capacity in the workplace and the storage in specific areas of the high capacity ones is a rule that may be implemented to put into practice this principle of prevention. In this case; the risk derived from storage and transference of chemicals should not be underestimated (see recommendations in sheets no. 11 and no. 7, respectively in chapter 3 of part I of these guidelines).

Suitable working procedures including arrangements for the safe handling, storage and transport within the workplace of hazardous chemical agents and waste containing such chemical agents.
When procedures are designed correctly, they can prevent unnecessary exposure. They are technically essential in some cases such as:

- performing operations involving critical risks. For example, an intermittent operation which can cause major environmental contamination will be carried out when the workshop is unoccupied, to avoid exposing workers not directly involved in this.
- in situations of unknown risk. For example, when implementing a process for which there are no precedents and whose risk assessment is a purely theoretical estimation. In such situations, the procedures will form part of the work permits which must restrict the performance of specified tasks to qualified workers.
- in operations in which the prevention measures are inadequate and the risk can be reduced or eliminated by a number of pre-established guidelines. For example, bringing the local extraction system into operation before starting a specific operation which requires this.

Table I.2 shows some specific measures which apply the general principles for prevention.

Table I.2 Application of the principles for prevention

GENERAL PRINCIPLES FOR PREVENTION	APPLICATION
Reducing to a minimum the number of workers exposed	• Limiting access to certain areas, which prevents the unnecessary exposure of workers carrying out other jobs. • Physical segregation of areas for carrying out certain operations.
Reducing to a minimum the duration and intensity of exposure	• Providing sufficient ventilation of premises. • Adapting process variables without reducing efficiency
Appropriate hygiene measures	• Suitability of eating and smoking areas.
Reducing the quantity of chemical agents	• Making available the quantity of chemical agents needed for the work in the workplace.
Provision of suitable equipment and safe maintenance procedures.	• Establishing conditions to be met by work equipment before purchase and drawing up maintenance operation protocols.
Design and organisation of systems of work at the workplace	• Eliminating or adapting operations where workers may come into contact with agents where such contact is not necessary.
Suitable working procedures	• Written guidelines for carrying out tasks detailing, step by step, safety requirements to be taken into account. • Supervision of the correct application of these written guidelines.

The application of these principles, together with the training and information actions stipulated in Directive 98/24/EC, may sufficiently reduce risks of little consequence (slight risks) although, in general, if the risk has not been eliminated, further specific measures suited to each situation will be necessary.

Tables A3.1 and A3.2 in Annex 3 to this Guide provide examples showing the difference between the application of general rules fundamentally affecting the organisation of work and specific prevention measures applying in both cases.

3. SPECIFIC PREVENTION AND PROTECTION MEASURES FOR CONTROLLING CHEMICAL RISKS

3.1 SPECIFIC PREVENTION AND PROTECTION MEASURES AND THEIR PRIORITISATION

If the general prevention strategy due to the application of the general principles set out in Article 5 of Directive 98/24/EC proves insufficient to reduce the risks arising from the presence of hazardous chemical agents, employers must apply the specific measures to which Articles 6, 7 and 10 refer. In applying these measures the employer may take into account the guidance provided in table I.3. This applies:

- to the actual chemical agent,
- to the process,
- to the workplace and/or
- to the work method.

In some cases, these measures will enable the risk to be eliminated, while in others they will only enable this to be reduced or will focus on worker protection. Table I.3 summarises the main specific measures applicable, with priority being accorded to those which eliminate risk rather than those which only reduce this, and to the latter rather than those whose purpose is to mitigate the consequences of the occurrence of the risk and to protect the worker. Thus, *the priority of the prevention measure is indicated by the rows and, within each row, from left to right*.

Brief indications on the use of each of these measures are given below in summary sheets. In some cases, these indications are accompanied by illustrations on the reverse. Some of the solutions in these sheets correspond to the COSHH Essentials control strategies. For example, Sheet 6 on local extraction corresponds to level 2 of the COSHH Essentials control strategy and Sheet 5 on containment to level 3.

Table I.3 Specific prevention measures and their prioritisation

Priority	Objective	Area of application			
		Chemical agent	***Process or Installation***	***Workplace***	***Work method***
1	*Risk elimination*	• Total substitution of the chemical agent	• Modification of the process • Use of intrinsically safe equipment(1)		• Automation
2	*Risk reduction-control*	• Partial substitution of the agent • Change of form or physical state(2)	• Closed process • Local extraction	• Safe storage • Segregation of dirty departments • Ventilation by dilution • Fire prevention	• Safe handling • Safe internal transport
3	*Worker protection*			• Eyebaths and showers • Fire protection • Explosion prevention and protection	• Respiratory, skin and eye PPE

(1) Applicable for eliminating the risk of fire or explosion.
(2) For example, handling of a solid material in a wet state, in the form of a paste or gel or encapsulation may reduce the inhalation risk.

1. SUBSTITUTION (TOTAL OR PARTIAL) OF THE CHEMICAL AGENT

Description
In accordance with the provisions of Article 6(2) of Directive 98/24/EEC, substitution of the hazardous chemical agent shall be the preferred specific measure for eliminating or reducing chemical risk. Substitution, however, poses two main problems which mean that its application is very often difficult:

1) Chemical agents which are technically viable as substitutes are not easy to find.
2) Technically viable substitutes may also be hazardous to a degree and this has to be taken into account.

The solution to the first difficulty depends on the technical characteristics of the process. The second problem can be solved by using any of the existing methods for substitution of chemical substances, such as that drawn up by the BIA (*Berufsgenossenschattliches Institut für Arbeitssicherheit*) which we will describe below.

Area of application
- A technically viable substitute exists
- Its hazard rating is lower than that of the hazardous chemical agent used.

Design basics
The BIA has drawn up a method for evaluating substitutes. Use of this method is recommended in those cases where no specific information is available as to which is the suitable substitute from the safety and health aspect.

The method is based on the analysis of the hazard rating of the chemical agent substituted by using the R phrases it has been assigned (Table I.4). Depending on these phrases, the chemical agent used initially and its potential substitute must be placed in one of the boxes in each of the five columns of the attached table. The substitute will be appropriate if it poses less of a risk than the chemical agent originally used, *in each of the columns*.

***Application example*:** in a particular process, the idea is that benzene should be substituted with toluene. The process is closed but there are possibilities of exposure when taking samples.

The R phrases applicable to benzene are: R11, R45, R48/23/24/25
The R phrases applicable to toluene are: R11Repr. Cat. 3; R63, R48/20-65, R38, R67

Toluene would be a suitable substitute for benzene as it is equal to or lower than this in all the columns, as shown in the table.

Level of risk	**Acute risk to health**	Chronic risk to health	Risk of fire and explosion	Potential exposure	Hazards associated with the process
Very high		**Benzene (R45)**			
High	**Benzene (R25)**		**Benzene, Toluene (R11)**	**Benzene (vapour pressure: 100 hPa)**	
Medium	**Toluene (R20)**			**Toluene (vapour pressure: 29 hPa)**	**Benzene, toluene**

Examples of successful substitutions abound in the history of industrial hygiene,. One of the classic examples is the replacement of white phosphorus by red phosphorus in the manufacture of matches, although it must be pointed out that this change took place in response to a tax problem and not to lower the risks of the process. This was, however, largely achieved. In the field of degreasing, there has been a series of well-known substitutions: from petroleum naphtha to carbon tetrachloride, which subsequently made way for halogenated hydrocarbons, which were in turn replaced by fluorinated hydrocarbons.
There have been other successful substitutions in the field of abrasives, where crystalline silica has been replaced by synthetic compounds such as carborundum, which is far less hazardous. The same may be said in the field of paint where solvents have been gradually substituted, in many applications, with water - which is not only less toxic but also much cheaper.

Table I.4 Columns model*

Level of risk	**Acute risk to health**	**Chronic risk to health**	Risk of fire and explosion	Potential exposure	Hazards associated with the process
Very high	**R26, R27, R28, R32**	**R45, R46, R49** * Preparations containing more than 0.1 per cent of carcinogenic substances from Categories 1 or 2.	**R2, R3, R12, R17**	**Gases** **Liquids with a vapour pressure above 250 hPa** Solids which generate dust **Aerosols**	**Open process** Possibility of direct contact with the skin **Application over a very large area.**
High	**R23, R24, R25, R29, R31, R35, R42, R43** **Sensitisers of the skin or respiratory tract** Preparations which contain skin or respiratory sensitisers in a concentration greater than or equal to 1% (in the case of gases, 0.2%).	**R40, R60, R61, R68** **Preparations which contain Category 1 or 2 substances toxic to reproduction in concentrations over 0.5% (in the case of gases, 0.2%)** **Preparations which contain more than 1% of Category 3 substances toxic to reproduction.**	**R1, R4, R5, R6, R7, R8, R9, R11, R14, R15, R16, R18, R19, R30, R44**	**Liquids with a vapour pressure between 50 and 250 hPa.**	
Medium	**R20, R21, R22, R34, R41, R64** **Simple asphyxiants**	**R62, R63** **Preparations which contain over 5% (in the case of gases, 1%) of Category 3 substances toxic to reproduction.**	**R10**	**Liquids with a vapour pressure between 10 and 50 hPa (except water)**	*** Closed process but with the possibility of exposure when filling, sampling or cleaning.**
Low	**R36, R37, R38, R65, R66, R67** Skin problems when working in humid environments.		Substances which are not very flammable (flash point between 55 and 100°C)	**Liquids with a vapour pressure between 2 and 10 hPa**	
Negligible	**Non-hazardous chemical agents**		Substances which are not flammable or have very low flammability (flash point above 100°C)	**Liquids with a vapour pressure below 2 hPa.** **Non-powdery solids.**	Leakproof equipment Closed equipment with local extraction at the emission points.

Level of risk	**Acute risk to health**	**Chronic risk to health**	Risk of fire and explosion	Potential exposure	Hazards associated with the process

*The table does not reproduce the column corresponding to the danger for the environment as this must be assessed by taking into account the national regulations of Member States.

2. USE OF INTRINSICALLY SAFE EQUIPMENT

Description

- This involves purchasing equipment designed and constructed in accordance with intrinsic safety criteria, with the manufacturer having planned for this to be used for the processing or transfer of products with certain physico-chemical properties (corrosiveness, flammability) or under working conditions which are particularly aggressive (e.g. for use in corrosive or very humid environments) or hazardous (e.g. in potentially flammable or explosive atmospheres). The "CE" marking of the equipment guarantees such performance.
- Similar criteria must be followed when the result of the risk assessment reveals the need to adapt equipment which is already installed and in use.

Area of application

- When it is anticipated that products handled or processed using this equipment, due to the intrinsic hazard posed by these (flammability or explosiveness) or due to particularly aggressive characteristics of the environment in which this equipment is installed (corrosiveness, potentially flammable or explosive atmospheres), may:
  - damage the equipment or some of its components, thus reducing safety and endangering workers;
  - lead to deflagration or explosions endangering workers
- In the case of flammable and explosive substances, where it cannot be guaranteed using other technical/prevention measures (e.g. ventilation) that the working atmosphere will be manifestly below the Lower Flammable Limit (LFL) and Lower Explosive Limit (LEL) respectively.

Technical basis

- Equipment used in handling and processing hazardous liquids must offer the physical and chemical resistance appropriate to the necessary work conditions and constraints.
  The design of reactors must facilitate sampling operations, reading of measuring instruments and safe manual product loading and emptying operations. Closed systems will be used wherever possible.
  In the event of possible failures (power cut, failure of regulation and control elements of the equipment, etc.), the necessary safety resources must exist to allow the identification of these failures and the continuation of the process under safe conditions.
  In operations on equipment in which spillages may occur, systems for the collection and drainage of spills to a safe place which can be easily cleaned shall be available.
- Machinery intended for use in potentially flammable or explosive atmospheres shall be powered by safe energy (totally pneumatic or hydraulic control systems and components). If electrical equipment is used, it shall have explosion-proof characteristics (Ex) or (EEx). The requirements of Directives 94/9/EC and 98/37/EC shall be met in all cases.

Maintenance

A preventive, and where possible predictive, maintenance programme is needed which ensures that the initial performance of the equipment as regards its reliability and safety will be maintained. With this in mind, the manufacturer's instructions contained in the Instruction Manual and, in the absence of this or in addition to this, good professional practice shall be followed.

Ascertainment of effectiveness

- Implementation of the necessary and planned maintenance operations will be checked and a documentary record will be made of these, specifying the results, the improvements to be incorporated, the deadlines and persons responsible for implementation, and the persons responsible for checking that these are effective.
- Safety inspections in addition to the established maintenance schedule will be planned, with a view to detecting possible equipment anomalies or malfunctions which may endanger workers.

3. AUTOMATION

Description
Automation consists of replacing the human operator in a process with mechanical or electronic devices. In this way, workers cease to be in contact with the hazardous chemical agents (exposure ceases) or are in contact for less time (exposure decreases) or are at a distance from the sources of exposure (intensity decreases). Automation entails changes in a process and may be partial or total. Total automation makes it possible to dispense with the presence of humans, except in the case of maintenance operations or one-off actions.

Examples:
- The use of robotised systems in spray painting operations, thereby replacing painters, eliminates human exposure in a work environment which is usually highly contaminated, both by organic paint solvents and by the metal oxides forming the pigments.
- The electrolytic chromium-plating process, which has traditionally entailed exposure to chromium VI, may be partly automated (use of hoists to fill and empty vats) so that the distance between workers and sources of contamination increases or the chromium-plating line may be totally automated so that exposure to hexavalent chromium is avoided.

4. CHANGE OF FORM OR PHYSICAL STATE

Description
When powdered substances are used, their tendency to pass into the environment (hence the risk associated with their use) can be reduced appreciably by modifying their physical form and using them in the form of granules, pellets or other similar, more compacted, forms.

Examples:

- Encapsulation of enzymes or plant health products
- Pellets and flakes instead of powdery products

5. CLOSED PROCESS OR CONTAINMENT

Description

- Enclosing the entire process or certain particularly contaminating operations is a good solution where chemical agents with a high or average hazard rating are involved.
- Enclosing the process consists of using a leakproof, or near-leakproof, physical casing within which the operations specific to the process take place without direct human participation.

Area of application

- Continuous or non-continuous processes of the type customary in the chemical, pharmaceutical or food industries.
- Highly contaminating operations when they form part of a process involving little contamination.

Design basics

Closed processes can be complex in their design as many of their elements must be installed to allow the process to be started and stopped, but they have no function at all during ordinary operation. An example of this is expansion vessels or valves used solely for the initial filling or emptying of circuits, or elements whose function is solely to facilitate repairs.

In containing specific operations, the same principles used for the design of local extraction hoods must be observed:

- hoods which enclose the source as much as possible
- hoods which are as close as possible to the source without obstructing the work
- the throughput must be sufficient to prevent the build-up of extracted particles or dust.

The containment design must pay particular attention to the problems of static electricity when flammable liquids are transferred and the possible formation of explosive atmospheres in those points of the process where this can occur.

Maintenance and checks

In the case of closed processes, attention must basically be paid to three types of problem:

- Loss of leakproofness: leaks which may appear at the discontinuities in the system, particularly at valves, flanges, joints, pump seals, sampling points, etc.
- Control of static electricity: using work processes which minimise its generation and the systematic use of earthing.
- Control of flammable atmospheres: it is very important to control the existence of flammable atmospheres (which may give rise to devastating explosions) by using instruments which allow their existence to be detected (explosion meters) and protective elements (see the ATEX Guide).

Application examples

Containment of the entire process is the usual solution used in processing industries (chemical, food, pharmaceutical) in which large quantities of chemical agents, at least some of which are appreciably hazardous, are handled. In these cases, the chemical agents are kept permanently within closed containers (reactors, heat exchangers, etc.) and are moved from one container to another via leakproof pipes.

The specific containment of certain operations is a standard measure applied at process entry and exit points (supply of raw materials, extraction of products, etc.) and when any operation is highly contaminating but forms part of a process whose other operations are not contaminating. The dosing of cytostatic drugs in a hospital or the painting of vehicle bodywork on a vehicle production line are examples of operations of this kind. In general, the containment of operations of this kind must be supplemented by the use of local extraction.

Reverse of sheet No 5 (Containment or enclosed process)

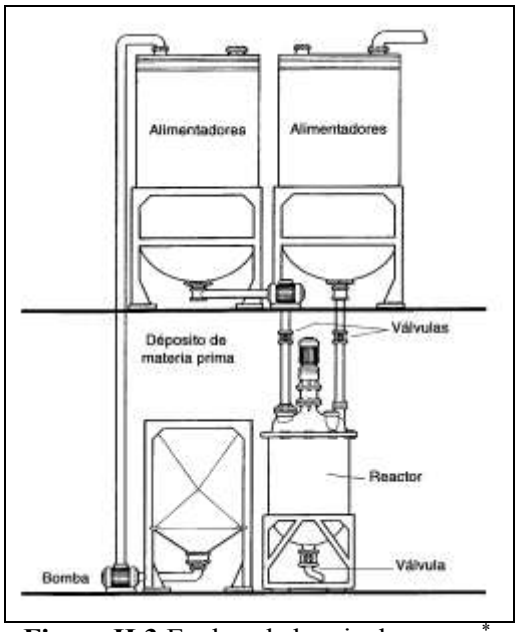


Figure II.3 Enclosed chemical process*
[key: Alimentadores = feed
Deposito de materia prima = raw material tank
Bomba = pump
Valvula(s) = valve(s)
Reactor = reactor]

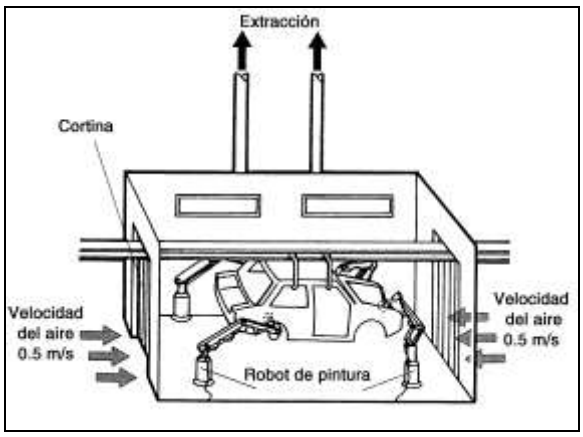


Figure II.4 Robotised spray booth*
[Key: Extracción = exhaust
velocidad del aire = airflow
Cortina = flexible screen
Robot de pintura = robot spray arms]

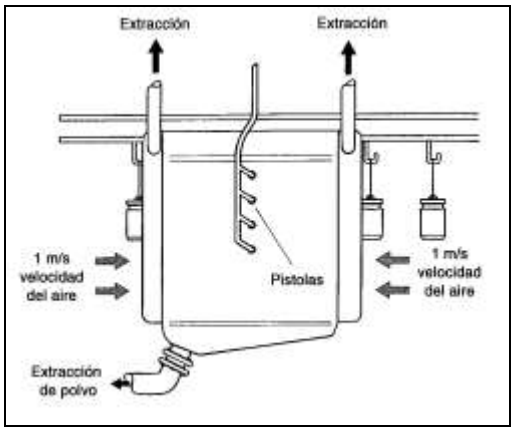


Figure II.5 Powder coating booth *
[Key: Pistolas = spray heads
Extracción de polvo = dust collection
Extracción = exhaust]

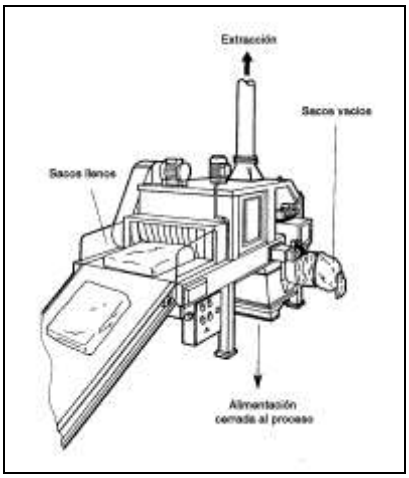


Figure II.6 Sack emptying machine*
[Key: Sacos llenos = whole sack feed
Sacos vacios = waste bag collection
Alimentación cerrada al proceso = closed feed to process]

* **Adapted from COSHH Essentials. HSE, 1999.**

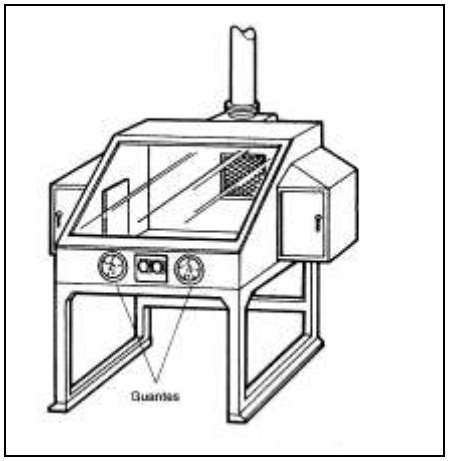


Figure II.7 Glove box*
[Key: guantes= glove ports

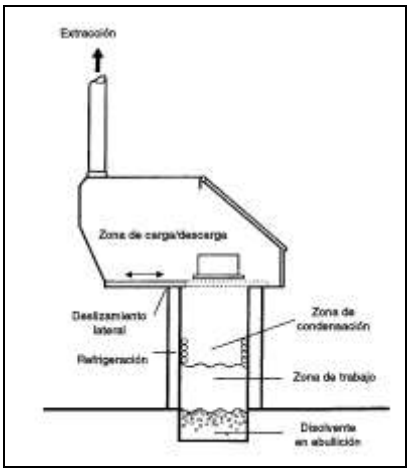


Figure II.8 Vapour degreasing bath*
[Key: extracción = exhaust
zona de carga/descarga = load/unload zone desli
zamiento lateral = automatic lid
zona de condensación = condensation zone
zona de trabajo = work zone
disolvente en ebullición = boiling solvent
refrigeración = cooling coils]

6. LOCAL EXTRACTION

DESCRIPTION

- Local extraction creates, by means of suction, a draught to capture the environmental contaminants in the immediate vicinity of the source generating these.
- Extraction is carried out as close as possible to the source of emission.
- It prevents the contaminant from dispersing into the environment and therefore avoids concentrations which are hazardous due to inhalatory exposure or due to the substance approaching the Lower Flammable Limit (LFL) or Lower Explosive Limit (LEL) for vapours and explosive powders respectively.
- When the option is available, local extraction supplied by the actual manufacturer of the equipment, as is usual with certain types of machinery, such as that in the timber industry, for example, is to be recommended. The same may be said in the case of certain portable tools which can produce dust, such as grinders, handsaws, etc.

Area of application

- For any level of toxicity of substances.
- Few sources of emission exist and their location is known.
- The amount of contaminant generated is high.
- Workers are near the sources.
- The dispersion of the contaminant is not uniform.

DESIGN REQUIREMENTS

- Its components are: hoods, ducts, purifiers and fans (Figure I.8).
- It must be designed and installed by a specialist. Some general design requirements are:
    - hoods which enclose the source as much as possible
    - hoods which are as close as possible to the source without obstructing the work
    - the air velocity in the immediate surroundings of the source will be chosen bearing in mind the characteristics of the contaminant and the movement of the air in the area
    - the extraction flow must not convey the contaminant towards the worker's respiration area
    - the throughput in the duct must be sufficient to prevent the build-up of extracted particles or dust
    - the fan will be chosen according to the flow which has to circulate and the loss of head in the system.
- The premises must have a forced air supply and a number of external air inlets which can provide a flow of external air which is equal to or greater than what is extracted by the local extraction system.

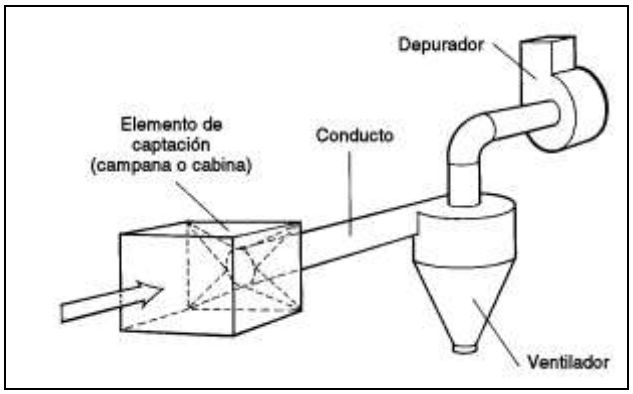
MAINTENANCE AND CHECKS

- Check of capture rates at the points where contaminants are generated. This check may be quantitative (anemometers or flow meters) or qualitative (smoke tubes or similar).
- Check of the flow drawn up by each hood (normally by measuring the static pressure at the hood or the velocity in the duct after the hood).
- Check of the physical integrity of the hoods and ducts. There must be no cracks, breaks, disconnected ducts, loose flanges, accumulation of dirt in ducts or in filters, etc.
- Check of pressures at significant points of the circuit (junctions between hoods and ducts, the purifier inlet and outlet, if there is one, and the inlet to the fan).
- Check of the fan and its mechanical components (casing, rotor, motor, bearings, drive belts, etc.).
- The user MUST NOT modify the system without the prior approval of its designer. In particular, no new branches must be added when installing additional machinery.

Application examples

Laboratory hood (Figure I.9), welding (Figure I.10), vats for the treatment of metals (Figure I.11), work tables for various operations, such as trimming castings (Figure I.12), painting booths (Figure I.13), etc.

Reverse of sheet No 6 (Local exhaust ventilation)



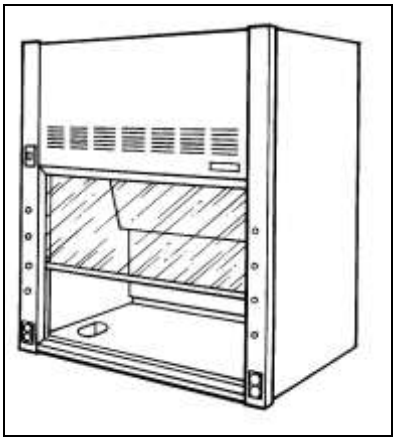
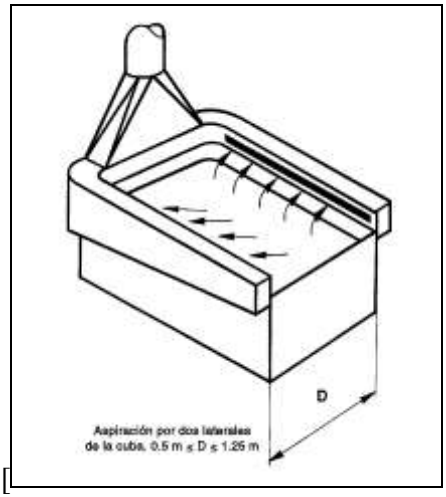


Figure II.9 Components of a local exhaust ventilation system **Figure II.10** Laboratory cabinet
[Key: Elemento de captación (campana o cabina) = capturing device
(hood or booth)
Conducto = duct
Ventilador = fan
Depurador = air cleaner]

Figure II.11 Welding operation. with Hood with movable arm.
[Key: Campana = hood]
de



[

Figure II.12 Electroplating tank lip extraction
[Key: Aspiración por dos laterales la cuba = lip extraction]

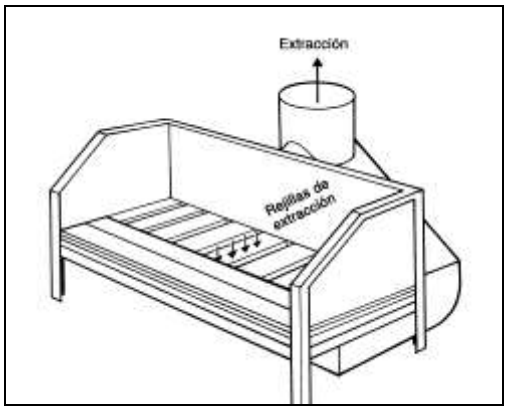


Figure II.13 Work table with local exhaust ventilation
[Key: Rejillas de extracción = extraction grilles
Extracción = exhaust]

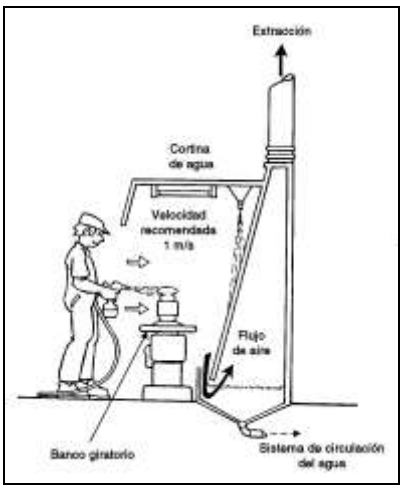


Figure II.14 Spray painting booth*
[Key: Extracción = exhaust
Cortina de agua = water spray
Velocidad recomendada = recommended airflow
flujo de aire = airflow
banco giratorio = rotatable pedestal
sistema de circulación de agua = water circulation system]

7. SAFE STORAGE OF HAZARDOUS CHEMICAL AGENTS (HCAs)

Description

- The employer is responsible for guaranteeing the safe storage of HCAs in the undertaking, whether in a specific enclosure intended solely for storage or in those situations which, due to process needs, require quantities of HCAs to be present at the workplace.
- The storekeeper or person responsible for the process area in which HCAs are stored must hold the information provided by the manufacturer or supplier of the HCA (SDS, labels), or from any other source, concerning the properties of the HCAs and must convey this clearly and precisely to workers exposed to these. From this information: work procedures must be established and their compliance checked; the perfect state of packaging or containers holding such HCAs must be checked; the storage plan must be drawn up and kept permanently updated, and the emergency plan for the store must be devised and updated.
- Workers must strictly apply the work procedures laid down and immediately inform the person in charge of any incidents or anomalies occurring in the course of their work. They must use the prescribed PPE.

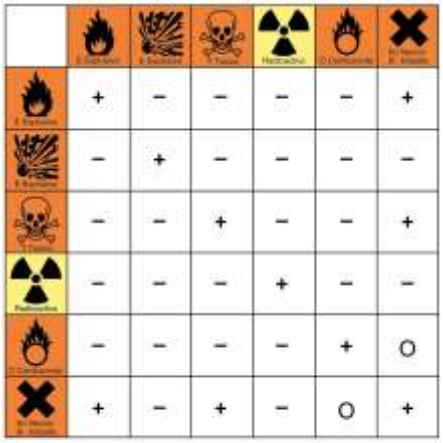
Management of stocks and organisation of the store

- The storage plan must allow the nature of the HCAs stored and their quantity and location in the store to be known rapidly and accurately so that prompt and effective action can be taken in the event of an incident (leak, spillage, fire, etc.). This plan must be kept permanently updated through a documentary record of incoming and outgoing stock.
- In terms of prevention, the main measure is maintaining HCA "stocks" at the lowest possible level. Once this principle has been accepted and adopted, the safety of the store requires a number of basic measures to be applied, including the following:
    - The safe siting of stores away from process areas or other hazardous areas in the undertaking (transformer substations, power plants, etc.) and from possible external interference (flooding, sabotage, etc.).
    - Products grouped by risk category, avoiding the combined storage of incompatible (Table I.6) or highly reactive HCAs. The different classes of HCA will be stored in separate areas, in the same area segregated by a fire-resistant partition or wall, or separated by distance (Figure I.14).
    - Setting and adhering to maximum quantities of stored chemicals and also maximum storage heights.
    - Products contained in secure containers (sufficient physical resistance, automatic closure, etc.) suitable for the HCA they contain (sufficient chemical resistance). Where appropriate, they will be approved or certified under the legislation of each country.
    - Means for guaranteeing recovery, retention and, when necessary, conveyance to reserve containers in the event of a leak or spillage of the stored HCAs (retaining trays, appropriate coverings for the floor and, at the perimeter, the lower part of partitions or walls of enclosures in order to guarantee that they cannot be penetrated by the liquid in the enclosure, drains and pipes to reserve containers, etc.). The above will also have to be taken into account, when necessary, for the recovery, retention or control of wastewater resulting from the fighting of fires.
    - Unobstructed access points and signed traffic routes and storage areas.
    - Control of access by persons and vehicles from outside the installation.
    - Evacuation routes and emergency exits which are unobstructed and signed.
    - Guaranteed product identification. Requirement for labelling and relabelling as necessary.
    - Precise work instructions for storage operations per se and any other operation usually performed in the store (opening and closing of containers, packaging, transferring, connecting and withdrawing tubes for filling containers, sampling, etc.).
    - Written action procedures in the event of incidents (leaks, spillages, emissions and similar).

Action procedures in the event of an emergency

- When, due to process needs, quantities of hazardous chemicals must be present in the workplace, these will be limited to the quantity strictly necessary for immediate work (never quantities in excess of those needed for the shift or working day) and will be placed in suitable containers, protected cupboards or special enclosures (Figure I.15). Generally speaking, they will comply with the applicable requirements described above.

Reverse of sheet No 7 (Safe storage)



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	–	–	+	–	–	+
	–	–	–	+	–	–
	–	–	–	–	+	O
	+	–	+	–	O	+

\+ Se pueden almacenar conjuntamente.
O Sólamente podrán almacenarse juntas, si se adoptan ciertas medidas específicas de prevención.
– No deben almacenarse juntas.

Table II.5 **Overview showing storage incompatibilities of hazardous substances.**

Key:

E Explosivo = E Explosive
T Tóxico = T Toxic
Radioactivo = Radioactive
O Comburente = O Combustive
Xn Nocivo = Xn Noxious
Xi Irritante = Xi Irritant

+	**may be stored together**
O	**may only be stored together if specific prevention measures taken**
–	**must not be stored together**

Examples of incompatible agents:
- **Oxidising agents with: inflammable substances, carbides, nitrides, hydrides, sulphides, alkylmetals.**
- **Reducing agents with: nitrates, chlorates, bromates, oxides, peroxides, fluoride.**
- **Strong acids with strong bases.**
- **Sulphuric acid with: cellulose, perchloric acid, potassium permanganate, chlorates.**

:

-
- **Example of** unstable substances:
- **Products that may decompose when stored for long periods: alkaline anhydrides, certain diazonium salts**
- **Substances that readily peroxidise: allylic compounds, vinylic compounds, styrene.**
- **Compounds that react violently on contact with air: phosphides, hydrides.**
- **Monomers that polymerise rapidly: vinyl acetate, styrene, acrylonitrile.**

Examples of incompatible agents:
- **Oxidising agents with: inflammable substances, carbides, nitrides, hydrides, sulphides, alkylmetals.**
- **Reducing agents with: nitrates, chlorates, bromates, oxides, peroxides, fluoride.**
- **Strong acids with strong bases.**
- **Sulphuric acid with: cellulose, perchloric acid, potassium permanganate, chlorates.**

Figure II.15 Separation by isolation or segregation

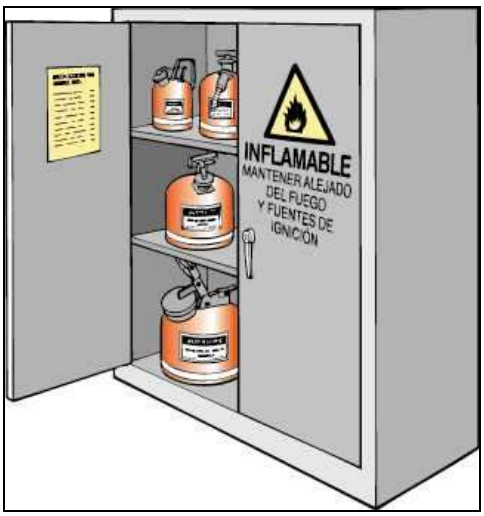

Figure II.16 Reinforced cupboard for storage
of flammable products

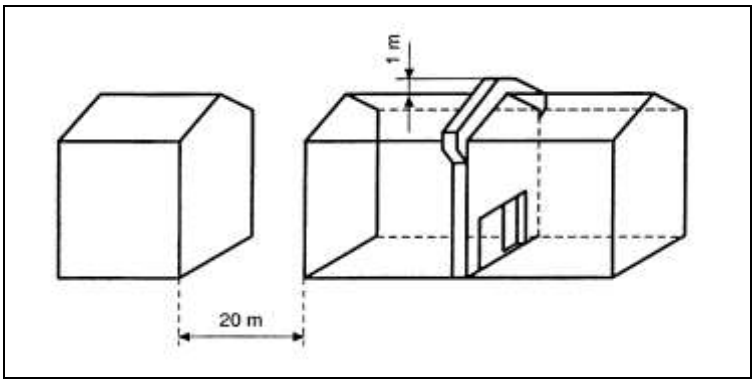

Figure II.15 Separation by isolation or segregation

8. SEGREGATION OF "DIRTY" DEPARTMENTS

Description

- Specific operations or processes which, due to their nature and because they involve intense mechanical action on materials, are particularly contaminating as they generate a large quantity of particulate matter.

- Therefore, in premises where operations such as metal cleaning, sawing of plastic, metal or wood, trimming of metal castings, grinding of solid substances and drilling of metals or wood are carried out, particles are released and spread through the environment.

- Also, work surfaces, tables, floors and machinery become covered with dust or fibres which, when mixed with lubricating oils, cleaning paste, resins, etc., continuously generate dirt.

Technical basis

It is practical to separate and contain this type of operation in premises segregated from the rest of the manufacturing area. The dispersal of contaminated air and dirt through other areas is prevented and ventilation and cleaning resources are concentrated in smaller spaces, thus increasing their effectiveness and reducing the cost of the actions undertaken.

9. GENERAL VENTILATION BY DILUTION

Description

- This consists of renewing the air of premises by supplying an appropriate quantity of clean external air and extracting a similar quantity of contaminated air.
- The air can enter naturally (doors, windows, etc.) (Figure I.16) or be forced (by means of fans) (Figure I.17).
- General ventilation is actually a principle for prevention (Article 5 of Directive 98/24/EC) rather than a specific measure. Therefore, general ventilation complying with the requirements established in Directive 89/654/EC on health and safety requirements for workplaces must always be guaranteed in workplaces. However, in some cases which we detail below, it may also be regarded as a specific measure for controlling risk and is therefore the subject of a sheet.

Area of application

- As a specific measure for controlling risk due to exposure, if this involves substances of low or medium toxicity by inhalation (LV > 100 ppm in the case of vapour or 5 mg/m³ in the case of particulate matter).
- Control of the risk of fire and explosion in containers and equipment by reducing the concentration of contaminant below the Lower Flammable Limit (LFL) and Lower Explosive Limit (LEL) in the case of vapours and explosive powders respectively.
- Control of smells and irritating substances by reducing the levels below the recommended limits of comfort.

Design requirements

- Specify systems for replacing extracted air.
- Dimension the heating or cooling system of the premises by taking into account the flow of ventilation air needed in the premises.
- The required ventilation flow must be calculated based on the rate of generation of the contaminant and the target environmental concentration to be maintained.
- If local extraction systems exist, calculation of the ventilation flow for the premises will take into account the requirements of those systems.
- Avoid the re-entry into the premises of extracted air by segregating the air outlets from possible inlets.
- Arrange the air inlets and outlets in such a way that the air circulation covers the entire premises, avoiding dead zones with little ventilation (Figures I.18, I.19, I.20).
- Take into account as ventilation air only the flow actually introduced into the enclosure from outside and not recirculated flows.
- Take account of the flow requirements of local extraction systems when calculating the general ventilation flow for the premises.

Maintenance and checks

- Follow the manufacturer's and/or installer's instructions (forced ventilation).
- Obtain the fullest possible information concerning installation from the manufacturer and/or installer.
- Do not close or obstruct the external air inlets during cold weather.
- Visually inspect possible damage to the system: broken ducts, fan blades, etc.
- Measure the environmental concentration of the contaminants after the system has been implemented.

Recommendations as to use

- Indicated for the ventilation of offices and premises for non-industrial use and industrial use, such as:
  - ventilation of workshops for processing metals, wood, etc.
  - ventilation of stoves, drying furnaces, pump or compressor rooms, etc.
- Limited use in controlling the risk of fire and explosion in premises (always as a measure supplementing other actions)
- Use not recommended:
  - if the quantity of contaminant generated is large
  - if workers are close to the contamination sources
  - if the dispersal of the contaminant is not uniform

Reverse of sheet No 9 (Dilution ventilation)

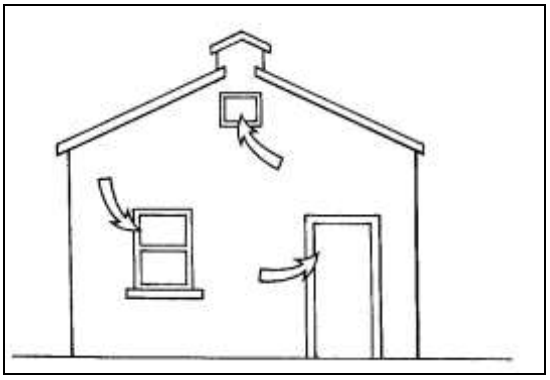

Figure II.17 Natural ventilation

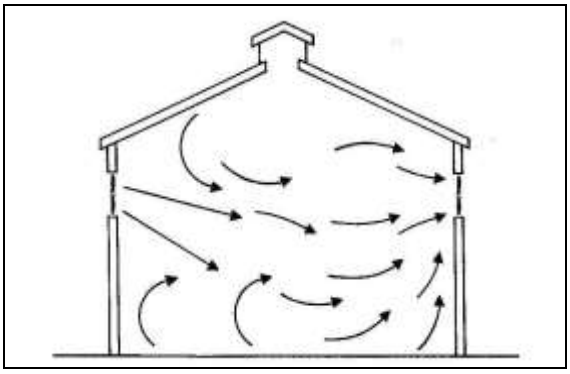

Figure II.18 Forced ventilation

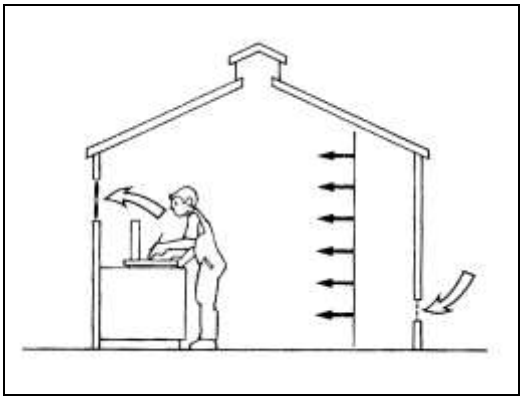

Figure II.19 Correct approach:
- Air distributed evenly throughout the area- Outlet is located near the emission source and the airflow moves the contaminant away from the worker's breathing zone

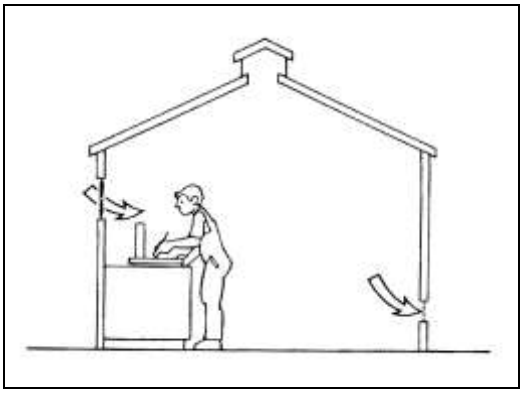

Figure II.20 Incorrect approach: - Clean air draws the contaminant towards the worker's breathing zone

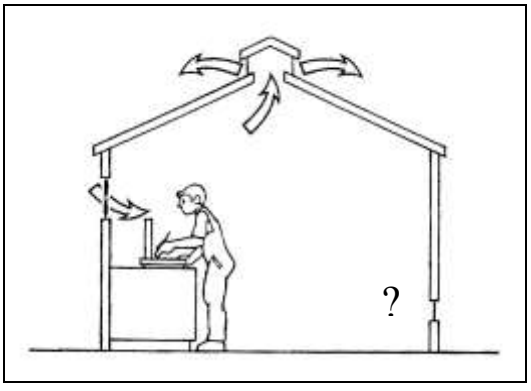

Figure II.21 Incorrect approach:
- There may be 'dead spaces' with poor or no ventilation- Clean air draws the contaminant towards the worker's breathing zone

There are 'dead spaces' with poor or no ventilation

10. FIRE PREVENTION

Objective

- To identify, for elimination or control purposes, fuels which, due to their physical state (gas, vapour, finely divided solid) and/or method of storage or use, can easily catch fire and also sources of ignition capable of providing the energy needed to initiate the reaction. On a local and exceptional basis, the objective may extend to control of the comburant (percentage of O_2 in the environment) (Figure I.21).

Fuel control measures

- Avoid the presence of substantial stockpiles of flammable substances in the workplace by reducing these to the minimum quantity needed to meet the needs of the process or operation to be carried out per working day or shift.
- The quantities of flammable liquids which must be stored in the work area should be kept in protected cupboards, duly marked with the indication and pictogram for "Flammable" and having a minimum fire resistance of 15 minutes (Figure I.15).
- Flammable liquids present in the workplace and their waste must be contained in airtight safety containers with automatic closures (Figure I.22).
- Operations involving flammable gases or liquids in which vapours (transfer, application by air brush, etc.) may be given off will be controlled using local extraction systems (see specific measure No 6: local extraction) and adequate general ventilation of the work area (see specific measure No 9: ventilation by dilution), in such a way that their environmental concentration is guaranteed to be well below the LFL.
- Hazardous concentrations of gases or vapours which may be generated will be checked using explosion meters.
- Transfers and other operations in which splashes or spillages may occur will be carried out in places and using specific means preventing these from occurring and ensuring, if necessary, their collection and drainage to a safe place under adequate ventilation conditions (0.3 $m^3/min.m^2$; never less than 4 m^3/min) with an alarm in the event of the system failing.
- Residues in equipment which has contained flammable or finely divided solid fuels, as well as their surroundings, will be cleaned prior to maintenance or hot repair operations.

Ignition source control measures:

- **Use of intrinsically safe work equipment. This will generally meet the requirements of Directive 98/37/EC and, specifically, those of Directive 94/9/EC.**
- **Loading, unloading or transfer operations will be carried out avoiding the generation of electrostatic charges (control of the rate of transfer, filling containers using a submerged tube, etc.) and facilitating their elimination through the equipotential earth connection of all equipment and containers (Figure I.23).**
- **The electrical installation and equipment will be protected from the risk of fire and explosion (Ex or EEx) in accordance with the electrical safety requirements in force in each country. Special attention needs to be paid to the use of mobile equipment and to the accessories used with or connected to this.**
- An exhaustive check of other sources of ignition will be established:

    - thermal (smoking, operations involving a flame or sparks, maintenance trolleys and similar)
    - mechanical (use of non-sparking tools in container opening or closing operations and in environments in which there may be hazardous concentrations or accumulations of flammable products; use of footwear without metal parts, etc.).
    - chemical (heat generated in exothermic reactions, co-existence of chemically unstable or reactive products, etc.)

Measures for the control of comburants:

These measures may be established in the case of flammable products in the liquid state or solid fuels in the powder state or residues of these where it is not possible to take any action on these. For this purpose, the process of inerting is essential when operations must be carried out for the maintenance or hot repair of equipment which has contained flammable or combustible chemical agents or finely divided solids and their elimination cannot be guaranteed.

Reverse of sheet No 10 (Fire prevention)

Figure II.22 Causes of fires
and preventive and protective measures
[Key: Combustible = fuel
calor = heat
reacción en cadena = chain reaction
aire = air
inicio = start
propagación = spread
consecuencias = consequences
prevención... = Prevention. Prevent fires starting
protección… = Protection. Limit the spread and consequences of the fire]

Figure II.23 Safety container for flammable liquids

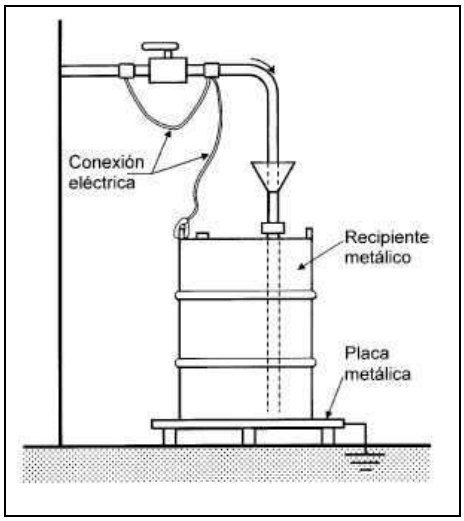

Figure II.24 Equipotential and earth connection for the transfer of flammable liquids
[Key: Conexión electrica = electrical connection
Recipiente metálico = metal container
Placa metálica = metal plate]

11. SAFE HANDLING OF HCAs

Description

- This consists of the handling of HCAs and their transfer, loading or unloading in production units.
- The equipment used will preferably be fixed and rigid (fixed piping) rather than mobile (containers, mobile piping, etc.).
- Mobile transfer equipment, both manual equipment and that activated by mechanical systems, must be compatible with the possible risks of the environment (fire, explosion and/or corrosion) and the materials from which this is manufactured must be compatible with the HCAs handled.
- Various HCA safe handling designs are shown in other specific measure sheets, such as 1.3, 1.6 and 1.24.

Area of application

- Frequent transfer of HCAs from large tanks, containers and packaging to others of a smaller capacity for their direct use in production processes.
- Use of mobile containers for loading/unloading process plant equipment.
- Transfer of HCAs from large tanks or containers to production processes using fixed or mobile piping with generally non-permanent connections.

Technical recommendations

- Only containers or packaging made of materials which are compatible with the products to be transported, which comply with the requirements for the carriage of dangerous goods by road and which have guaranteed stability and resistance with regard to the possible aggression to which they may be subject during use will be used.
- Transfers will preferably be carried out using manually- or mechanically-operated suction pumps. As far as possible, transfer by gravity between containers will be avoided when exposure or contact with HCAs may result. If this type of transfer is used, the feed container will be placed horizontally on a fixed or mobile frame or cradle with locking wheels.
- For the unloading of flammable products, all metallic elements will be equipotentially connected and earthed. In the case of liquids, the feed container will be fitted with a discharge valve with an automatic closure.
- In the transfer by gravity of flammable liquids, funnels will be used whose throat must reach to at least 1 cm from the bottom of the container to be filled.
- In all transfer operations, collecting trays will be placed below points of possible spillage.
- In the transfer of solid products, the generation of dust and uncontrolled entry of air into containers will be avoided. To this end, manual transfer will be avoided and equipment guaranteeing the airtightness or enclosure of the process will preferably be used (e.g. dosing devices using rotating valves, double gates, helicoidal screw conveyors, etc.).
- Fixed or mobile piping systems must have guaranteed stability, resistance and reliability with regard to possible mechanical and HCA aggression.
- Connections and fixed and mobile piping must be specific to and different for each type of HCA. Joints and unions must be leakproof, resistant to the product and in good condition.
- In piping, welded unions, rather than non-threaded unions or those with flanges, will preferably be used, especially indoors.
- Piping in which an HCA under pressure or likely to generate pressure may be retained will be protected by safety valves with an outlet to a safe place (absorption tower, flare, treatment plant, etc.).
- Piping needing this will have devices for the collection of spillages or leaks.
- Mobile piping will be fitted with a mechanism allowing emptying before disconnection.
- No operations for transferring HCAs will be carried out using equipment or devices which have leaks or defects (dents, pores, blisters, defective flanges, etc.).
- A safety shower and an eyebath must be placed in the vicinity of the transfer areas.
- Effluent, spillages and treatment products will be stored in specific areas in certified containers which are duly marked, physically segregated and classified by compatibility and reactivity.

Maintenance and inspection

- Periodic inspection and maintenance of all internal transfer elements, with any incidents being recorded.
- Repairs to transfer equipment will be carried out by staff authorised by the user or manufacturer.

- In fixed or mobile piping, before a connection is made for loading and/or unloading the product, the absence of spillages or leaks will be checked. The means of detection will be compatible with the HCA contained.
- All internal transfer equipment will be kept clean and in good condition, with its specific use being duly marked, and it will be properly stored when not in use.
- Broken equipment or equipment in poor condition will be withdrawn immediately for replacement or repair as appropriate.
- The presence of leaks and/or spillages will be checked periodically using specific detection equipment.
- **Systems and equipment for the treatment of effluent will be inspected periodically and whenever necessary, with the reagents needed for their operation being repaired and/or replaced.**

12. SAFE INTERNAL TRANSPORT

Description

- The means used, whether manual or mechanical, must be safe for humans and compatible with the products handled.
- The equipment used will preferably be fixed and rigid (fixed piping) rather than mobile (containers, mobile pipe, etc.).

Area of application

- Transfer of HCA between different areas or processes of the undertaking, especially when extremely flammable or corrosive or very toxic products are transported.

Technical basis

- Only containers or packaging made of materials which are compatible with the products to be transported, which comply with the requirements for the carriage of dangerous goods by road and which have guaranteed stability and resistance with regard to the possible aggression to which they may be subject during use will be used.
- For transporting containers or packaging using mobile equipment, means of sufficient strength and with load securing points will be used.
- Fixed or mobile piping systems must have guaranteed stability, resistance and reliability with regard to possible mechanical and HCA aggression.
- Connections and fixed and mobile piping must be specific to and different for each type of HCA. Joints and unions must be leakproof, resistant to the product and in good condition.
- In piping, welded unions, rather than non-threaded unions or those with flanges, will preferably be used, especially indoors.
- Buried piping for flammable, toxic or corrosive liquids will be avoided, except where the piping has a double sheath and leak control.
- Piping in which an HCA under pressure or likely to generate pressure may be retained will be protected by safety valves with an outlet to a safe place (absorption tower, flare, treatment plant, etc.).
- Piping needing this will have devices for the collection of spillages or leaks.
- No operations for transferring HCAs will be carried out using equipment or devices which have leaks or defects (dents, blisters, cracks, defective flanges, etc.).
- Mobile transport equipment will have protection systems which are appropriate for areas classified as hazardous (fire, explosion or corrosion) and for the transported HCAs.

Maintenance and inspection

- Periodic inspection and maintenance of all internal transfer elements, with any incidents being recorded.
- Repairs to motorised transport equipment will be carried out by the manufacturer's authorised staff.
- In fixed or mobile piping, when making a connection for loading and/or unloading the product, the absence of spillages or leaks will be checked using a detection system compatible with the HCA contained.
- The devices for transporting and controlling HCAs must be marked visibly, legibly and indelibly with the date of their last inspection.
- Equipment in poor condition will be withdrawn immediately for replacement or repair.
- The presence of leaks and/or spillages will be checked periodically using specific detection equipment.
- Systems and equipment for the treatment of effluent will be inspected periodically and whenever necessary, with the reagents needed to ensure the continuity of their operation being repaired and/or replaced.

13. EYEBATHS AND SHOWERS

Description

- Safety showers (Figure I.24) are the most common emergency system for situations involving splashing with a risk of chemical burns and even where clothing catches fire.
- Eyebath fountains (Figure I.25) are designed to allow the rapid and effective decontamination of the eyes and basically consist of two sprayers or nozzles between 10 and 20 cm apart which are capable of providing a jet of drinking water for washing the eyes or face, a washbasin, between 25 and 35 cm, provided with the corresponding wastepipe, a system for floor- or wall-fixing and a foot- (pedal) or elbow-operated actuator.

Characteristics of showers

- The shower must provide a flow of water which is sufficient to soak the individual completely and immediately. The water supplied must be drinkable and care must be taken to ensure that this is not cold (preferably between 20 and 35°C) so as to avoid the risk posed by chilling a burn victim who is in a state of shock, and also because the reluctance to use cold water leads to insufficient elimination of the contaminants if showering time is shortened. This should also have a wastepipe (which enormously facilitates maintenance).
- The shower head must be of a diameter sufficient to totally soak the person (20 cm), with large holes preventing their obstruction due to the formation of limescale. The distance from the floor to the base of the shower head must allow a person to stand upright (for example, from 2 to 2.3 metres). The distance between the wall and the shower head must be sufficient to accommodate two people (for example, not less than 60 cm) where necessary. It is also recommended that the distance from the floor to the push button does not exceed 2 m.
- The opening valve must be of the rapid-action type, so conventional taps must not be used. The push button/actuator must be easy to grasp. The most suitable models are those with a triangular actuator linked to the system by a fixed bar (better than with a chain). Foot-operated push buttons are not usually used due to the ease of stepping on them inadvertently, resulting in the involuntary activation of the system, and the risk of tripping over them; systems activated by standing on a platform are an exception.
- The installation's stopcocks must be located in a place not accessible to staff, so as to avoid the supply being permanently cut off in the event of leaks or other faults which must, moreover, be immediately reported and repaired. Stopcocks will therefore only be shut off when the repair is carried out.
- It is useful to have an acoustic or visual alarm system available which is activated when the equipment is used. This therefore allows other staff to be made aware of the problem and they can then give assistance. Showers located in cloakrooms or toilets may perform the subsidiary functions of safety showers, especially in the case of small laboratories and for minor burns or splashes on clothing since, being out of sight, they allow the victim to remove their clothing without any concern.

Characteristics of eyebath fountains

- **The jet provided through the nozzles must be low pressure so as to not to cause unnecessary injury or pain. As has been indicated in the case of the shower, the water must be drinkable and it is recommended that it should be lukewarm. The same precautions will be taken with the stopcocks of the installation as in the case of safety showers.**

Reverse of sheet No 13 (Showers and eye wash units)

Figure II.25 Safety shower

Figure II.26 Eye-wash unit

14. PROTECTION AGAINST FIRE

Objective

- The prevention measures described in Sheet 10, although essential, are inadequate as they do not ensure under all circumstances exhaustive control of the risk and, accordingly, supplementary protection measures aimed at minimising the consequences of an incident occurring (Figure I.21) must be adopted.

Protection measures to be considered

- A distinction should be made between:
  - passive protection measures (structural protection of load-bearing members to guarantee a particular fire stability; sectorisation and compartmentalisation of areas with a different level of risk guaranteeing a specific fire resistance and the use of construction and coating materials having a known behaviour in the presence of fire)
  - measures for fighting fire properly speaking (human detection or automatic fire detection installations; flexible and reliable means of transmitting the alarm; fire-fighting equipment, whether portable or fixed, manually activated or automatically discharged, and evacuation routes which are sufficient in number, of a proper size and adequately distributed).

- The full set of fire-fighting measures which may be required under Directive 98/24/EC must comply with the framework of legal requirements specific to each country in terms of fire protection.
- Regardless of that stated in the above point, a number of specific measures which must be considered are set out below:
  - Ensure that the structural protection of the load-bearing members gives the enclosure or building a particular fire stability.
  - Check the vertical or horizontal spread of the effects of the fire and, for this purpose, work areas with a fire risk will be segregated from the rest of the premises by forming a fire sector with a fire resistance appropriate to the existing thermal load. Sectorisation will be carried out using distance or by compartmentalisation with fire partitions and walls (Figure I.26).
  - Guarantee effective detection, whether human or automatic, and provide installations which ensure rapid and reliable transmission of the alarm.
  - Have adequate and sufficient fire-fighting installations, whether fixed or portable, manually activated or automatically discharged. The extinguishing agents must be appropriate and must have the capacity to extinguish the HCA to be extinguished (e.g. use of type B for flammable liquids) and given the area of application (e.g. avoid using CO_2 in external areas). It shall also be guaranteed that extinguishing agents which are not compatible with the HCA shall not be used (e.g. do not use water to extinguish alkalines).
  - The number and state of the evacuation routes will allow rapid and safe evacuation of the occupants.
  - When necessary, the fire-fighting means and access to the evacuation routes will be signed according to the provisions of Directive 92/58/EEC.
  - Guarantee the removal of fire-induced smoke by means of outlets or other means of extraction (Figure I.27).

Reverse of sheet No 14 (Fire protection)

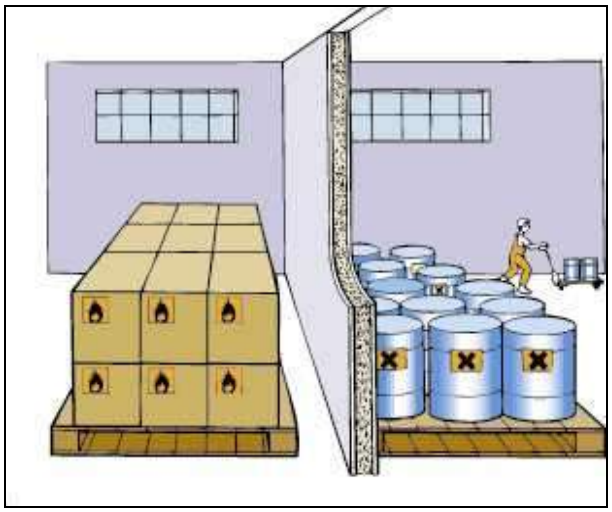

Figure II.27 Segregation with fire-resistant partition

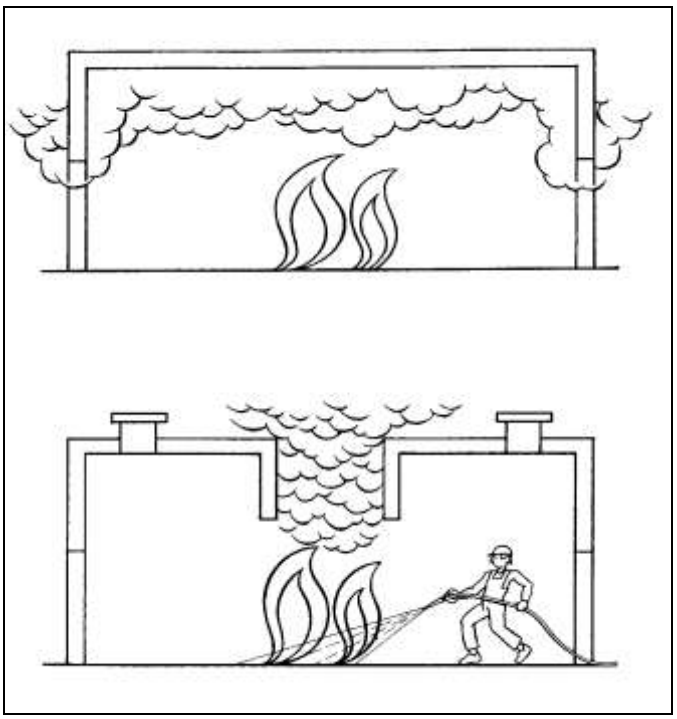

Figure II.28 Smoke outlets

15. PREVENTION AND PROTECTION AGAINST EXPLOSIONS

The prevention and protection measures to be considered for improving the protection of the health and safety of workers exposed to the risks arising from explosive atmospheres are not dealt with in this Guide as this risk is specifically regulated by Directive 1999/92/EEC. (See its corresponding implementation guide).

The essential safety and health requirements which may be demanded in respect of protection apparatus and systems for use in potentially explosive atmospheres are regulated and developed in Directive 94/9/EC.

16. PERSONAL PROTECTIVE EQUIPMENT

Area of application

Personal protective equipment (PPE) constitutes the last barrier between the hazardous chemical agent and the worker, so its use is limited to the following cases:

- when the collective or organisational prevention and protection measures applied are insufficient or technically non-viable.
- when the collective prevention and protection measures which are appropriate cannot be adopted immediately and provisional recourse must be had to said personal protection.
- in one-off operations or a situation which may not justify permanent measures being established, provided that the use of PPE guarantees a level of protection equivalent to that which would be afforded by the measures it replaces.
- whenever emergency, rescue or self-rescue situations arise.

Types of protective equipment

- respiratory (see specific measure 16.1)
- eyes (see specific measure 16.2).
- **skin (gloves and clothing protecting against chemical risk) (see specific measure 16.3)**

Reverse of sheet No 16.1 (Respitory protection equipment)

Figure II.34 Filtering facepiece

FigureII.35 Half-mask

Figure II.36 Full-face mask

Figure II.37 Mouthpiece assembly

Figure II.38 Self-contained breathing apparatus

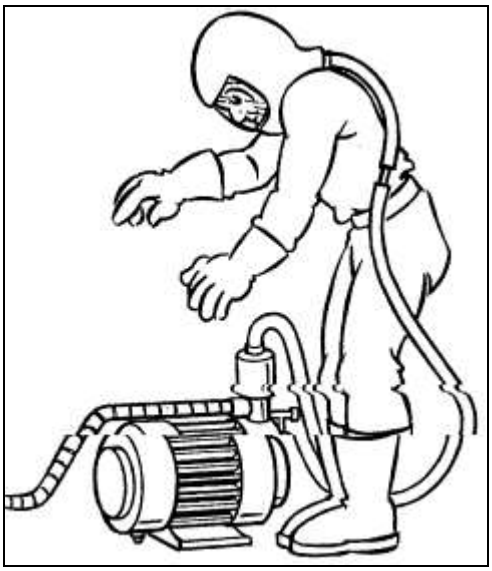

Figure II.39 Airline breathing apparatus

16.2 EYE PERSONAL PROTECTIVE EQUIPMENT

Use

To prevent contact between the eyes and chemical agents in a liquid, solid or gaseous state which may damage them or which may be absorbed through the conjunctiva. These circumstances can occur:

- Due to liquid or solid particles being splashed or sprayed.
- Due to gases escaping.
- Due to high concentrations of solid or liquid aerosols, gases or vapours being present in the work environment. Normally, this will coincide with the need to use respiratory PPE. In this case, a mask or hood, or goggles accompanying the mask, if appropriate, will be used.

See Figures I.34 and I.35.

Marking of the frame

Code	Application
No code	For unspecified mechanical risks and UV, IR and visible radiation.
3	Against drops and splashes of liquids.
4	Against dust with a particle size greater than 5 μm.
5	Against gases and vapours, mists, fumes and dust with a particle size less than five μm.
8	Against an electric arc produced in an electrical short circuit.
9	Against splashes of metals and penetration of incandescent solids.

Remarks

- Garments must possess the CE mark and certification and, as regards protection from chemical risks, the number three or five, as applicable, marked on the frame as the protection index.
- The *information leaflet* in which the manufacturer indicates the features of the garment - types, protection indexes and substances against which it protects - and the conditions of storage, cleaning, sizes, etc., must be consulted.
- Provision must be made for their replacement in the appropriate time frame.

Reverse of sheet No 16.2 (Eye protection equipment)

Figure II.40 Face shield

Figure II.41 Safety goggles

16.3 SKIN PROTECTIVE EQUIPMENT - GLOVES AND CLOTHING FOR PROTECTION AGAINST CHEMICAL RISK

Use

Gloves (Figure I.36) and garments for skin protection, such as aprons, gaiters or suits, are used when contact between the skin and work clothing and chemical substances must be avoided, either because these can be absorbed through the skin or because they can damage it.

As far as the chemical risk is concerned, protective gloves and garments are made to be airtight (protection against penetration at the joins, seams, etc.) and resistant to the substance passing through the material which forms the glove or garment (protection against permeation). The latter protection depends on the substance against which it protects and is not permanent but has a maximum effective life. In this way, each pair consisting of the material of which the garments are made and the chemical product against which it protects has a level of protection. There are six levels of protection.

	Protection index	Breakthrough time
Level of protection against permeation *	1	>10 minutes
	2	>30 minutes
	3	>60 minutes
	4	>120 minutes
	5	>240 minutes
	6	>480 minutes

** refers to a specific substance (e.g. ethanol, etc.)*

Types of suit

Suits, which cover the whole body, are further classified as follows:

TYPE OF SUIT	FEATURES	
TYPE 1A	Respiratory protective equipment within the suit	Impermeable to chemicals in the gaseous or vapour state. Cover the whole body, including gloves, boots and respiratory protective equipment
Type 1b	Respiratory protective equipment outside the suit	
Type 1c	Connected to a breathable air line.	
Type 2	Similar to those of Type 1c but less airtight at the seams	
Type 3	Impermeable to chemicals in the liquid state (jet or pressure)	
Type 4	Impermeable to sprayed chemicals	
Type 5	Impermeable to chemicals in the form of solid particles (dust)	
Type 6	Impermeable to small liquid splashes	

Remarks

Garments must possess the CE mark and certification and the protection symbol against chemical risk shown below.

Chemical risks

Example:

Protection index	Chemical agent
3	Ammonia 25%
2	Cyclohexylamine
0	Diethylether
6	Acetic acid

The *information leaflet* in which the manufacturer indicates the features of the garment - types, protection

Reverse of sheet No 16.3 (Hand protection equipment)

Figure II.40 Safety gloves

3.2 PREVENTION MEASURES DURING THE PRODUCT'S LIFE CYCLE

As stated in this chapter, chemical risk is defined by the *hazard rating* of the agent (physico-chemical or toxicological properties and its physical form) and by its *conditions of use*. For this reason, if substitution of the agent is not possible, the technical and organisational measures to be taken, according to a specified order of priority, will be directed towards establishing conditions of use in which the risk is minimised. This must be considered over the entire life cycle of products, from manufacture to disposal and treatment subsequent to use. The above must be taken into account from the perspective offered by two of the main axes of the current and future actions of the European Union in this area.

The *first* of these, which is more general in nature, is the Green Paper on Integrated Product Policy (COM(2001) 68 final) which proposes to establish a new growth paradigm and a higher quality of life through wealth creation and competitiveness on the basis of greener products. It also proposes a strategy to strengthen and refocus product-related environmental policy to promote the development of greener products.

An Integrated Product Policy is an approach which seeks to reduce the environmental impact of products throughout their life cycle, from the mining of raw materials to production, distribution and use, and waste management. This really means promoting the idea of the life cycle throughout the economy (including services, whose use can reduce the consumption of products), within all product-related decisions, together with other criteria such as functionality, health and safety.

The *second axis* is defined by the White Paper on the Strategy for a future Chemicals Policy (COM (2001) 88 final), whose overriding goal is sustainable development. Insofar as it refers to the purpose of this Guide, the above document points out that both manufacturers and importers, just like industrial users and producers of substances and preparations, should be responsible for all the safety aspects of their products and will be obliged to assess the safety of their products *for the part of the life cycle* to which they contribute, including disposal and waste management. The document likewise includes, among the research priorities, that of improving life cycle assessment methodologies for chemicals.

For this reason, and in the case of "extremely worrying" substances, the risk assessment submitted to the authorities to obtain authorisation from the latter to market the product shall cover the entire life cycle of the product. All this is established within a new chemical control system known as REACH (Registration, Evaluation and Authorisation of CHemicals) to be applied throughout the Community.

With reference to the scope of Directive 98/24/EC, the life cycle stages of products are as indicated below:

- Conception and design of the product: includes considering the chemical risk prior to manufacturing new products and processes.
- Production: the principles of minimisation as regards both the consumption of energy and natural resources and the generation of waste should be assumed, including the phase of use and disposal of the actual product in the final stage of its life.
- Handling: moving the product within the undertaking.
- Storage: on the producer's premises and/or in logistical stores.
- Packaging, including the secure identification of the product and the disposal of packaging.
- Distribution and sale.
- Use of the product by the customer, whether professional or private, as an end product or as a raw material for a new process.
- Disposal and treatment of the product: this takes place at the end of the product's life and may include processing prior to its disposal. The waste will have to be disposed of in a way which does not give rise to new risks to worker safety and health.

The analysis of the risks generated at each stage of a product's life cycle goes beyond the context of the undertaking manufacturing this. The end product for one company may be the raw material for another; it

must therefore be used as indicated by the manufacturer, which is why the flow of information between both parties and close collaboration where professional users are involved are essential.

The final stage of the cycle also entails risks for the environment which may be generated by the disposal and treatment of the product after its use. However, it is beyond the scope of this Guide to deal with this aspect.
It should be remembered that the principles for prevention mentioned in Chapter 2 are applicable whatever the case; as regards the specific prevention measures developed in Chapter 3, those most appropriate according to the stage in question in the product's life cycle must be chosen.

PART II

HEALTH SURVEILLANCE OF WORKERS EXPOSED TO LEAD AND ITS IONIC COMPOUNDS

1. HEALTH SURVEILLANCE OF WORKERS EXPOSED TO HAZARDOUS CHEMICAL AGENTS

For the purposes of Directive 98/24/EC, and therefore for the purposes of this Guide, health surveillance means "the assessment of an individual worker to determine the state of health of that individual, as related to exposure to specific chemical agents at work" (Article 2(f)).

Individual health surveillance (also referred to as medical surveillance) consists of the performance of tests and the application of medical procedures in respect of each worker in order to detect and assess any changes in his or her state of health or to adapt a person's job to his or her personal characteristics. This surveillance may be carried out through medical examinations (most common), although this is only one of the possible ways. Other ways are: health questionnaires, interviews, pre- and post-exposure tests, etc.

To this individual approach should be added the *collective approach* whereby individual data are compiled, analysed and interpreted for use in the planning, development and assessment of health protection and promotion programmes.

Employers' obligations with regard to protecting the health and safety of workers against risks relating to chemical agents and health surveillance include:

1. *Assessing the risks by taking into consideration the conclusions to be drawn from health surveillance studies, where available (Art. 4(1)).*
2. *Updating the risk assessment when the results of health surveillance show this to be necessary (Art. 4(2) and Art. 10(4)).*
3. *Reviewing the measures adopted to eliminate or reduce risks taking into account the results of health surveillance (Art. 10(4)).*

The steps below must be followed when establishing a health surveillance programme:

1. *Deciding, in light of the Directive, whether a health surveillance programme is required.*
2. *Determining appropriate procedures and frequency.*
3. *Providing the material and human resources for this surveillance to take place.*
4. *Ensuring workers and their representatives can appropriately participate and have suitable information.*
5. *Applying the necessary prevention measures in line with the results obtained.*
6. *Reviewing the effectiveness of the prevention measures applied.*

Without prejudice to the provisions of Article 14 of Directive 89/391/EEC or to specific or more stringent European or national provisions and national practice, the employer shall adopt measures to ensure the *appropriate* health surveillance of workers where the results of the assessment described in Article 4 of Directive 98/24/EC reveal a risk to health and also for lead and its ionic compounds under the conditions specified in Annex II, where these have a binding biological limit value.

According to Article 10 of Directive 98/24/EEC, health surveillance will be deemed *appropriate* when the following conditions are *simultaneously* met:

- the exposure of the worker to a hazardous chemical agent is such that an identifiable disease or adverse health effect may be related to the exposure. Existence of a relationship between the chemical agent in question and damage to health; *and*
- there is a likelihood that the disease or effect may occur under the particular conditions of the worker's work, *and*
- the technique of investigation is of low risk to workers.

2. Nature of THE effectS OF exposure to lead AND its ionic compounds

An accumulation of lead in the body will have effects in workers. In the workplace, lead is mainly absorbed through the respiratory tract (while breathing) and the digestive system (while eating, drinking and smoking in the workplace). Around 90-95% is carried by the red blood cells. It builds up in the body and is mainly eliminated through the kidneys. Lead may take many months to be eliminated from the body and it particularly builds up in the bones.

The central nervous system (particularly the brain) is the most sensitive to exposure to lead. Other effects described in workers exposed to lead and its ionic compounds are: impairment of peripheral nerves and the kidneys, anaemia, raised blood pressure and colic and abdominal pains. Separate mention should be made of lead's potential effect on reproduction such as infertility, miscarriage, foetal death, low birth weight, premature birth, or neurobehavioural effects in children due to exposure in the mother's uterus or during breastfeeding.

3. CONTENT OF HEALTH SURVEILLANCE

We can divide the health surveillance programme for workers exposed to lead into two distinct parts: biological monitoring and medical examinations.

In line with Annex II to Directive 98/24/EC, medical surveillance is carried out if:

- *exposure to a concentration of lead in air is greater than 0.075 mg/m³, calculated as a time-weighted average over 40 hours per week, or*
- *a blood-lead level greater than 40 μg Pb/100 ml blood is measured in individual workers.*

The medical examination should include:

- A full *work history* which, in addition to data on past exposure to lead, takes into account the use of personal protective equipment or clothing and all those practices which may increase exposure to the agent, such as inadequate hygiene habits or eating, drinking or smoking in the workplace. This history must include the *environmental monitoring* data for the job carried out by the worker since he or she was assigned to this.

- A *clinical history* that explores previous history and current effects on target organs such as the blood, nervous system, digestive system, kidneys and reproductive system. It is especially important to collect information on smoking, alcohol intake, medication and exposure to lead outside work. Some of the symptoms to be kept under surveillance when monitoring workers exposed to lead and its compounds are: fatigue, loss of appetite, abdominal pains or colic, constipation, metallic taste, depression or feeling low, irritability, difficulty in concentrating or with memory, personality changes, headaches, feeling of pins and needles or tingling in the limbs, muscular weakness, joint pains, loss of interest in sex and difficulty in having children.

- The *physical examination* must focus on the digestive and cardiovascular systems (including taking the blood pressure) and also on the nervous system.

- *Lead in blood* (PbB): the determination of lead in the blood serves two main purposes: on the one hand, as a *supplement to the environmental monitoring* (assessment of exposure) and, on the other, as a *tool of occupational medicine* integrated in the health surveillance of exposed workers. Due to their

importance, both points are specifically covered in another section. Persons responsible for the health surveillance of workers should also be responsible for developing and applying the biological monitoring programme, regardless of the use made of this within the undertaking. Close co-operation should be maintained at all times with industrial hygiene experts and confidentiality should be ensured at all times in terms of test conclusions, in accordance with national practice and recognised ethical guidelines.

- Other tests: taking into account exposure conditions and also the individual characteristics of exposed workers, certain complementary examinations discussed below may be included *on a non-routine basis and always on medical advice*:

  Blood pressure:
  Data currently available suggest a link between exposure to lead and an increase in blood pressure. Because the measurement is harmless, simple to carry out and cheap, its use is recommended particularly due to its usefulness in health surveillance in its collective long-term aspect. Its frequency will be established on the basis of medical advice according to age and time and level of exposure. It would be advisable for the blood pressure to be taken in the initial examination and during the periodic examination. The minimum frequency for taking blood pressure (which would apply to normotensive workers with PbB figures below 40 µ/100 ml) would be once a year.

  Haematocrit/haemoglobin
  Another of the effects of lead is the generation of anaemia due to the increased destruction of red blood cells and the inhibition of haemoglobin synthesis. For this reason, the inclusion of tests to determine haemoglobin concentration and the haematocrit value in venous blood may be considered. Workers with an iron deficiency (an anomaly commoner among women) and workers with a PbB in excess of 50 µ/100 ml are more susceptible to anaemia. It would also be appropriate to consider including, in the initial examination, other tests such as the study of blood content or other erythrocyte parameters in order to detect alterations such as a glucose-6-phosphate dehydrogenase deficiency or thalassemia minor; these are frequent problems in Mediterranean countries and in the African and South-East Asian populations which may worsen with exposure to lead.

  Zinc protoporphyrin (PPZ)
  Given that levels of PPZ are indicators of long-term effects, testing them could be useful as an addition to the PbB test when there are discrepancies between environmental and biological values, especially when it has been observed that the cessation of exposure in intermittent exposures leads to a decrease in PbB, with high levels of PPZ being maintained.

  Kidney function tests
  Both kidney function and structure can be affected by the action of lead. One of the biggest problems in the use of kidney function tests is that many of them show significant changes only when function has decreased by more than half, which serves to determine the severity and monitor development of the injury, but does not meet the requirement of early detection which is vital in preventive examinations. The use of tests such as levels of N-acetyl-glucosaminidase or ß-2-microglobulin in urine to monitor certain groups on account of the level and time of exposure may be considered.

  Study of the effects on the nervous system
  There are tests for the early detection and assessment of these effects. Basically, these are of two types: neurobehavioural and electrophysiological. Both types must be used in a way which is compatible with the clinical history and with an appropriate physical examination and monitoring.

  Other indicators

Other indicators have been described, such as lead in urine, erythrocyte ALAD activity, delta-aminolevulinic acid, levels of coproporphyrin in urine and even the concentration of lead in the hair. The advantages and disadvantages of such tests will depend on the specific exposure situation. Their usefulness will always be complementary and they must never be established as the alternative to lead in blood but as a complement to it.

Health surveillance must be designed to detect workers who are particularly sensitive to lead and its ionic compounds, whether permanently or temporarily, for example: workers of childbearing age, pregnant or breastfeeding workers, workers with changes in target organs, etc. Their detection will allow, as far as possible, the worker's job to be adopted to their condition by establishing special prevention measures required to preserve their health.

The medical examination is an ideal opportunity to inform workers and reinforce their knowledge about the risks associated with lead and the hygiene measures which are essential to minimise exposure and which are in the worker's hands: not to drink, smoke or eat in the workplace; washing of hands, arms and face and scrubbing of nails before eating, drinking and smoking; showering after work; correct use of personal protective garments assigned to their job, etc.

4. Biological monitoring of workers exposed to lead and its IONIC compounds

4.1 general Characteristics

In general terms, biological monitoring may be defined as the measurement and assessment of chemical agents in the workplace, their metabolites or their early non-pathological effects in an appropriate biological medium from the exposed person. The aim is to evaluate exposure and risks to health by comparing values obtained with an appropriate reference.

The chemical agent itself, the product of its conversion by the body, its metabolites or the biochemical change resulting from the reported effects, all of which may be measured, are called *indicators*.

The *biological media* most commonly used are blood, urine and expired air. However, one or more biological media may be used for the biological monitoring of each individual chemical agent - and others may not. The actual portion taken from these biological media from an individual in order to carry out measurements is the *sample*.

The measurement *result* reveals the individual's level of exposure and identifies whether or not the worker is in a situation of risk to their health when a *biological limit value* established for this contaminant is available, using an appropriate application criterion for this purpose.

In terms of their level of significance, the results of biological monitoring and their assessment do not differ essentially from those obtained using environmental monitoring methods because both types provide information that relates, as already indicated, to actual worker exposure and to the potential risk to health under certain conditions and not the workers' state of health at the current time or in the future.

Biological monitoring measures an individual's internal exposure and, as stated previously, can be subject to two different focuses: collective (as a complement to environmental monitoring) and individual (as a tool of occupational medicine, integrated within health surveillance). Their principal indications are summarised in Table II.1.

Table II.1 Applicability of biological monitoring

APPROPRIATE FOR	NOT APPROPRIATE FOR
• Confirmation of the results of an environmental assessment when this raises doubts, for example if it is difficult to obtain representative environmental measurements. • Detection of potential absorption by routes other than the respiratory tract. The initial risk assessment, based exclusively on environmental data, may be changed as a result. • Assessing the effectiveness of using personal protective equipment or other prevention measures introduced. • Detection of non-work exposures (environmental, domestic, in leisure activities, etc.) • Detection of individuals with a possible physical work overload in a group of workers theoretically operating under the same conditions. • Detection of exposures which, while not constituting a risk, could be reduced by improving work and personal hygiene habits.	• Monitoring exposure to chemical agents for which reliable indicators are not available. • Automatically replacing environmental monitoring of exposures to chemical contaminants which penetrate exclusively by inhalation. • Evaluating the state of a worker's health, even though a clear relationship with this may exist. • Making a clinical diagnosis of a disease. • Evaluating risks or effects due to acute exposures • Determining the work source of the contaminant analysed.

4.2 DETERMINATION OF LEAD IN BLOOD

The general aspects of biological monitoring which have just been mentioned constitute the basis for applying this method of prevention to workers exposed to lead and its ionic compounds. Lead in blood is the parameter of choice.

In its implementation stage, attention must be paid to the following technical aspects:

- Workers who must be subject to this monitoring
- Dates of implementation
- Sampling, storage and transport
- Analysis
- Receipt of results and quality control
- Definition of measures according to the results obtained
- Communication of information

In Annex 6 to this Guide, appropriate methods are proposed for taking samples and analysing lead and its ionic compounds in blood and air.

Bearing in mind that lead in blood is the most representative indicator of the state of dynamic balance reached between environmental lead and that in the body *when certain conditions are fulfilled* and that,

based on the results of the PbB test, *decisions* of some importance *must be taken*, it is obvious that reliable values must be obtained, with extreme care being taken in the sampling, collection and transport procedures and in the analysis process.

Use of the biological limit value as a reference is only correct when the following conditions are met:

1) exposure is maintained in a stable pattern throughout a given period (several months) prior to the biological monitoring,
2) the worker's body has actually achieved this balance when the blood sample is taken. In other words, no events have occurred which have prevented this balance from being achieved, or have distorted it, such as major physiological or pathological changes.

If biological monitoring were to be carried out on exposed workers without these conditions being met, the results obtained might not be representative of their real exposure and might lead to a misleading conclusion with regard to the assessment and true extent of the risk such workers faced.

Another essential issue is that of the requirements under which this test must be carried out so that the results obtained comply with the expectations regarding their usefulness in order to evaluate exposure to this metal or its ionic compounds and the risk to the health of specific workers arising from this.

In practice, there are two types of requirement which must be fulfilled: management and technical. As regards the laboratory, the management requirements range from the organisation of the actual laboratory, through the adoption of documentation control and quality systems, *inter alia*, to the system of internal audits. The technical requirements range from the staff, installations and methods of testing and calibration to the quality assurance of the result. Collectively and individually, these requirements are applied in EN-DIS 15189:2003 on the accreditation of test and calibration laboratories and, accordingly, may be appropriate for determining lead in blood.

Key factors for assessing the competence of an analytical laboratory:

- Compliance (if required) with the specific legislation applicable,
- Availability of storage and transport protocols,
- Appropriate equipment and qualified staff,
- Technical quality accreditation,
- Participation in inter-laboratory quality control programmes.

4.3 BIOLOGICAL MONITORING AS A TOOL OF OCCUPATIONAL MEDICINE

Bearing in mind that certain studies link the PbB level to certain effects on target organs (Table II.2), knowing the concentration of lead in the blood can allow guidance criteria to be established for deciding the frequency of health surveillance and also cut-off values to be established for proposing job changes or the biological limit value for particularly sensitive workers. The recommendations of this section must be reviewed and adapted to the specific conditions of exposure and characteristics of the protected population.

Table II.2 Blood-lead level and observed effects on health [17].

Reference criteria	Lowest level of observation of effect (µg/dl)	Effects on the blood	Neurological effects	Renal effects	Effects on the respiratory apparatus	Effects on offspring	Cardiovascular effects	Priority level
	100-120		Acute encephalopathy	Chronic nephropathy				
	80	Anaemia						
Directive 98/24/EC	70				Infertility (women)	Compromise of the reproductive capacity of the female foetus		
	50	Decrease in haemoglobin						
	40	Increase in ALAU	Neurobehavioural and peripheral nerve effects	Early signs of nephrotoxicity	Infertility (men)			Directive 98/24/EC
BEI-ACGIH[18] SCOEL[19]	30					Spontaneous abortions due to paternal exposure. Premature birth and reduction in weight at birth	Increase in blood pressure	
	25-30	Increase in PPZ ♂				Functional changes in newborn infants		
	15-20	Increase in PPZ ♀						
	< 10	ALAD inhibition						

[17] This table has been drawn up on the basis of Figure 1 included in the SCOEL/SUM/83 final report of January 2002, "Recommendation of the Scientific Committee on occupational exposure limits for lead and its inorganic compounds", and the sheet corresponding to lead and its ionic compounds in the ACGIH's "Documentation of the biological exposure indices - 2001".
[18] Biological exposure indices – American Conference of Governmental Industrial Hygienists.
[19] Scientific Committee on Occupational Exposure Limits.

Particularly sensitive
The occupational exposure limit value for lead and its ionic compounds, which is binding at Community level, reflects "in addition to the factors considered when establishing indicative occupational exposure limit values, … feasibility factors" (Article 3(4) of Directive 98/24/EC). For this reason, if data relating to neurotoxicity, nephrotoxicity and reproductive toxicity are taken into account, more restrictive criteria must be applied in certain groups requiring special protection. These groups will obviously be pregnant or breastfeeding women and young people, but may also be any worker who shows any condition or characteristic which may imply a greater likelihood of suffering from some effect of exposure, such as male and female workers of childbearing age, those with fairly serious renal, neurological or haematological problems, those with a raised body burden on account of earlier exposures, etc.: therefore, any circumstance which, on medical advice, represents a major risk to the health of the worker in question or his/her offspring.

Change of job
When damage has been caused to the health of a worker which is manifested either through an identifiable disease or through a number of harmful effects, or a binding biological limit value has been exceeded, Directive 98/24/EC (Art. 10(4)) establishes certain obligations for the employer, including that of taking into account the advice of qualified specialists or the competent authority in implementing the measures provided for in Article 6 to eliminate or reduce risk, "including the possibility of assigning the worker to alternative work where there is no risk of further exposure."

Removing certain workers from a job according to the PbB level is a protection measure which seeks to prevent possible damage to health from occurring. It is appropriate that, before carrying this out, the PbB should be checked again within the following 15 days. The PbB cut-off levels at which a change of job for exposed workers is recommended will depend primarily on age, sex and certain personal characteristics:

- Exceeding the biological limit value stated in Annex II to Directive 98/24/EC will entail the compulsory removal of the worker from his/her job and the performance of bimonthly checks until that value is, on two consecutive occasions, below the binding biological limit value applicable at European or national level (if this is stricter than the European value).

- The non-existence of "safe" values to avoid repercussions on the foetus or breastfed child which exposure to lead and its ionic compounds may have makes it advisable to avoid exposure on the part of a pregnant or breastfeeding worker to levels of lead in blood which are greater than those of the general reference population. For this reason, care is to be taken to see that this level is not exceeded and that the job is immediately changed if it is.

- In workers under 18, the cut-off level will be 50 µg/dl, using the same reinstatement procedure as for adult workers.

- The prevention of changes affecting reproduction in the exposed population (among both men and women) makes it advisable to reduce the exposure of workers of childbearing age to lead as far as possible. In the case of men, the critical period will be 90 days prior to conception. In women, keeping lead levels in blood below 25-30 µg/dl would be advisable, given that lead is also a toxin which accumulates in the body and can be released during pregnancy or breastfeeding.

Type and frequency of health surveillance
Bearing in mind that health surveillance identifies whether prevention and protection measures adopted are really protecting workers' health, its content and frequency must be adapted so that, at key times, the data needed to ascertain this can be obtained.

Prior to exposure
Before assigning a worker to a job involving exposure to lead or its ionic compounds, a medical examination covering the specific objectives of the prevention programme and serving as a reference for the development of the worker's health to be studied over the course of time will have to be undertaken. It would be appropriate to include the following tests: blood pressure, haematocrit and haemoglobin, and any other test deemed necessary for detecting particularly sensitive workers, in addition to that described in Section 3 (work and clinical history, specific physical examination and determination of lead in blood). Repetition of the PbB until the worker has reached the balance referred to earlier is of particular interest.

Frequency
The minimum frequency for those workers whose blood-lead level (PbS) or air-lead level (PbA) is greater than 40 micrograms/100 ml or 0.075 mg/m^3 will be yearly in the case of the medical examination, and half-yearly in the case of biological monitoring.

Depending on the results obtained, this frequency may temporarily or permanently change to being half-yearly, quarterly, monthly etc., at all times on medical advice and in line with the clinical findings, personal characteristics and specific conditions of exposure. Complementary tests such as PPZ or neurobehavioural tests may be circumstantially added to the basic contents of the tests in order to clarify any discrepancies or previous results.

Circumstantial
This category would include those medical examinations prompted by damage appearing in one or more workers from a homogeneous risk group due to changes in work exposure (either due to sporadic problems or to changes in exposure conditions) or due to temporary or permanent changes in a worker's personal characteristics.

All those tests deemed appropriate for the early detection of the possible effects of these changes must be added to the basic survey. In particular, in pregnant or breastfeeding women, whose exposure is comparable to the exposure of the general reference population or below 30 micrograms/100 ml (always selecting the most favourable option), PbB determinations must be carried out at least every three months.

For this reason, it is advisable to apply the recommendations summarised in Table II.3, always on medical advice, according to the circumstances of exposure and an individual's characteristics, and to improve the health protection of workers.

Table II.3 Recommendations on health surveillance and biological monitoring

<table>
<tr><th>PbB in µg/100 ml
Worker category*</th><th>> value for reference population or 40</th><th>41-50</th><th>51-60</th><th>61-70</th><th>≥ 70</th></tr>
<tr><td>Workers in general</td><td>Recommendation: HS[1] and BM[2] on medical advice</td><td colspan="2">HS and BM compulsory

Recommendation: yearly HS and BM every six months</td><td>Recommendation: Review of working conditions and changes, yearly HS or more frequently on medical advice, quarterly BM</td><td>Review of working conditions and changes (compulsory)
Recommendation: Removal from job***, yearly HS or more frequently on medical advice, quarterly BM</td></tr>
<tr><td>Pregnant women who have recently given birth or are breastfeeding</td><td colspan="5">Recommendation : Removal from job**</td></tr>
<tr><td>Under 18</td><td>Recommendation: HS and BM on medical advice</td><td>Recommendation: Review of working conditions and changes, yearly HS and quarterly BM</td><td colspan="3">Recommendation: Removal from job***, yearly HS or more frequently on medical advice and bimonthly BM</td></tr>
</table>

* Health surveillance will be subject to the worker's individual characteristics in each case.

** Return to work will take place when the risk to the woman, foetus or breastfed infant has ceased and the doctor in charge decides that this is the case.

*** Return to work will take place when the PbB value is less than the binding biological limit value at European or national level, preferably on two consecutive occasions (within an interval of two months)

[1] HS: Health Surveillance

[2] BM: Biological Monitoring

PART III

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ANNEXES

ANNEX 1

R AND *S* PHRASES AND THEIR COMBINATIONS

R risk phrases

R1	Explosive when dry.
R2	Risk of explosion by shock, friction, fire or other sources of ignition.
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition.
R4	Forms very sensitive explosive metallic compounds.
R5	Heating may cause an explosion.
R6	Explosive with or without contact with air.
R7	May cause fire.
R8	Contact with combustible material may cause fire.
R9	Explosive when mixed with combustible material.
R10	Flammable.
R11	Highly flammable.
R12	Extremely flammable.
R14	Reacts violently with water.
R15	Contact with water liberates extremely flammable gases.
R16	Explosive when mixed with oxidising substances.
R17	Spontaneously flammable in air.
R18	In use, may form flammable/explosive vapour-air mixture.
R19	May form explosive peroxides.
R20	Harmful by inhalation.
R21	Harmful in contact with skin.
R22	Harmful if swallowed.
R23	Toxic by inhalation.
R24	Toxic in contact with skin.
R25	Toxic if swallowed.
R26	Very toxic by inhalation.
R27	Very toxic in contact with skin.
R28	Very toxic if swallowed.
R29	Contact with water liberates toxic gas.
R30	Can become highly flammable in use.
R31	Contact with acids liberates toxic gas.
R32	Contact with acids liberates very toxic gas.
R33	Danger of cumulative effects.
R34	Causes burns.
R35	Causes severe burns.
R36	Irritating to eyes.
R37	Irritating to respiratory system.
R38	Irritating to skin.
R39	Danger of very serious irreversible effects.
R40*	Limited evidence of a carcinogenic effect.
R41	Risk of serious damage to eyes.
R42	May cause sensitisation by inhalation.

R43	May cause sensitisation by skin contact.
R44	Risk of explosion if heated under confinement.
R45	May cause cancer.
R46	May cause heritable genetic damage.
R48	Danger of serious damage to health by prolonged exposure.
R49	May cause cancer by inhalation.
R50	Very toxic to aquatic organisms.
R51	Toxic to aquatic organisations.
R52	Harmful to aquatic organisms.
R53	May cause long-term adverse effects in the aquatic environment.
R54	Toxic to flora.
R55	Toxic to fauna.
R56	Toxic to soil organisms.
R57	Toxic to bees.
R58	May cause long-term adverse effects in the environment.
R59	Dangerous for the ozone layer.
R60	May impair fertility.
R61	May cause harm to the unborn child.
R62	Possible risk of impaired fertility.
R63	Possible risk of harm to the unborn child.
R64	May cause harm to breastfed babies.
R65	Harmful: may cause lung damage if swallowed.
R66	Repeated exposure may cause skin dryness or cracking.
R67	Vapours may cause drowsiness and dizziness.
R68	Possible risk of irreversible effects.

* Recently amended. Previously had the meaning of the current R68 which was added due to this change. This amendment must be taken into account in cases of labels or safety data sheets which have not been updated.

Combination of R phrases

R14/15	Reacts violently with water, releasing extremely flammable gases.
R15/29	Contact with water releases toxic, extremely flammable gas.
R20/21	Harmful by inhalation and in contact with skin.
R20/22	Harmful by inhalation and if swallowed.
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed.
R21/22	Harmful in contact with skin and if swallowed.
R23/24	Toxic by inhalation and in contact with skin.
R23/25	Toxic by inhalation and if swallowed.
R23/24/25	Toxic by inhalation, in contact with skin and if swallowed.
R24/25	Toxic in contact with skin and if swallowed.
R26/27	Very toxic by inhalation and in contact with skin.
R26/28	Very toxic by inhalation and if swallowed.
R26/27/28	Very toxic by inhalation, in contact with skin and if swallowed.
R27/28	Very toxic in contact with skin and if swallowed.
R36/37	Irritating to eyes and respiratory system.
R36/38	Irritating to eyes and skin.
R36/37/38	Irritating to eyes, respiratory system and skin.
R37/38	Irritating to respiratory system and skin.
R39/23	Toxic: danger of very serious irreversible effects through inhalation.
R39/24	Toxic: danger of very serious irreversible effects in contact with skin.
R39/25	Toxic: danger of very serious irreversible effects if swallowed.
R39/23/24	Toxic: danger of very serious irreversible effects through inhalation and in contact with skin.
R39/23/25	Toxic: danger of very serious irreversible effects through inhalation and if swallowed.
R39/24/25	Toxic: danger of very serious irreversible effects in contact with skin and if swallowed.
R39/23//24/25	Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.
R39/26	Very toxic: danger of very serious irreversible effects through inhalation.
R39/27	Very toxic: danger of very serious irreversible effects in contact with skin.
R39/28	Very toxic: danger of very serious irreversible effects if swallowed.
R39/26/27	Very toxic: danger of very serious irreversible effects through inhalation and in contact with skin.
R39/26/28	Very toxic: danger of very serious irreversible effects through inhalation and if swallowed.
R39/27/28	Very toxic: danger of very serious irreversible effects in contact with skin and if swallowed.
R39/26/27/28	Very toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.
R42/43	May cause sensitisation by inhalation and skin contact.
R48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation.
R48/21	Harmful: danger of serious damage to health by prolonged exposure in contact with skin.
R48/22	Harmful: danger of serious damage to health by prolonged exposure if swallowed.

R48/20/21	Harmful: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin.
R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed.
R48/21/22	Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed.
R48/20/21/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation.
R48/24	Toxic: danger of serious damage to health by prolonged exposure in contact with skin.
R48/25	Toxic: danger of serious damage to health by prolonged exposure if swallowed.
R48/23/24	Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin.
R48/23/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed.
R48/24/25	Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed.
R48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R68/20*	Harmful: possible risk of irreversible effects through inhalation.
R68/21*	Harmful: possible risk of irreversible effects in contact with skin.
R68/22*	Harmful: possible risk of irreversible effects if swallowed.
R68/20/21*	Harmful: possible risk of irreversible effects through inhalation and in contact with skin.
R68/20/22*	Harmful: possible risk of irreversible effects through inhalation and if swallowed.
R68/21/22*	Harmful: possible risk of irreversible effects in contact with skin and if swallowed
R68/20/21/22*	Harmful: possible risk of irreversible effects through inhalation, in contact with skin and if swallowed.

* Prior to the amendment of R40 and the addition of R68, all these phrase combinations contained R40 instead of R68.

S safety phrases

S1	Keep locked up.
S2	Keep out of the reach of children.
S3	Keep in a cool place.
S4	Keep away from living quarters.
S5	Keep contents under ... (appropriate liquid to be specified by the manufacturer).
S6	Keep under... (inert gas to be specified by the manufacturer).
S7	Keep container tightly closed.
S8	Keep container dry.
S9	Keep container in a well-ventilated place.
S12	Do not keep the container sealed.
S13	Keep away from food, drink and animal feedingstuffs.
S14	Keep away from ... (incompatible materials to be specified by the manufacturer).
S15	Keep away from heat.
S16	Keep away from sources of ignition - No smoking.
S17	Keep away from combustible material.
S18	Handle and open container with care.
S20	When using do not eat or drink.
S21	When using do not smoke.
S22	Do not breathe dust.
S23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer).
S24	Avoid contact with skin.
S25	Avoid contact with eyes.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S27	Immediately remove all contaminated clothing.
S28	After contact with skin, wash immediately with plenty of ... (to be specified by the manufacturer).
S29	Do not empty into drains.
S30	Never add water to this product.
S33	Take precautionary measures against static discharges.
S35	This material and its container must be disposed of in a safe way.
S36	Wear suitable protective clothing.
S37	Wear suitable gloves.
S38	In case of insufficient ventilation, wear suitable respiratory equipment.
S39	Wear eye/face protection.
S40	To clean the floor and all objects contaminated by this material, use ... (to be specified by the manufacturer).
S41	In case of fire and/or explosion do not breathe fumes.
S42	During fumigation/spraying wear suitable respiratory equipment (appropriate wording to be specified by the manufacturer).
S43	In case of fire, use ... (indicate in the space the precise type of fire-fighting equipment. If water increases risk, add – 'Never use water').
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S46	If swallowed, seek medical advice immediately and show this container or label.
S47	Keep at temperature not exceeding ... °C (to be specified by the manufacturer).
S48	Keep wet with ... (appropriate material to be specified by the manufacturer).
S49	Keep only in the original container.
S50	Do not mix with ... (to be specified by the manufacturer).
S51	Use only in well-ventilated areas.
S52	Not recommended for interior use on large surface areas.

S53	Avoid exposure - obtain special instructions before use.
S56	Dispose of this material and its container at hazardous or special waste collection point.
S57	Use appropriate container to avoid environmental contamination.
S59	Refer to manufacturer/supplier for information on recovery/recycling.
S60	This material and its container must be disposed of as hazardous waste.
S61	Avoid release to the environment. Refer to special instructions/Safety data sheets.
S62	If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label.
S63	In case of accident by inhalation: remove casualty to fresh air and keep at rest.
S64	If swallowed, rinse mouth with water (only if the person is conscious).

Combination of S phrases

S1/2	Keep locked up and out of the reach of children.
S3/7	Keep container tightly closed in a cool place.
S3/9/14	Keep in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer).
S3/9/14/49	Keep only in the original container in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer).
S3/9/49	Keep only in the original container in a cool, well-ventilated place.
S3/14	Keep in a cool place away from ... (incompatible materials to be indicated by the manufacturer).
S7/8	Keep container tightly closed and dry.
S7/9	Keep container tightly closed and in a well-ventilated place.
S7/47	Keep container tightly closed and at a temperature not exceeding ... °C (to be specified by the manufacturer).
S20/21	When using do not eat, drink or smoke.
S24/25	Avoid contact with skin and eyes.
S27/28	After contact with skin, immediately remove all contaminated clothing, and wash immediately with plenty of ... (to be specified by the manufacturer).
S29/35	Do not empty into drains; dispose of this material and its container in a safe way.
S29/56	Do not empty into drains; dispose of this material and its container at hazardous or special waste collection point.
S36/37	Wear suitable protective clothing and gloves.
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S36/39	Wear suitable protective clothing and eye/face protection.
S37/39	Wear suitable gloves and eye/face protection.
S47/49	Keep only in the original container at a temperature not exceeding ... °C (to be specified by the manufacturer).

ANNEX 2

SIMPLIFIED RISK ASSESSMENT METHODOLOGIES

Simplified methodologies may be of much help (specially for small and medium interprises) in order to carry out the initial risk assessment and to determine the need for implementing control measures. As shown in picture I.5 of these Guidelines, the risk assessment process goes on, the most times, making a detailed assessment, unless the detected risk in the initial step was slight. Thus; *a priori*; these methodologies do not constituted an alternative to a detailed risk assessment but they make a first diagnosis of the situation/ Some of them give recommendations on the type of measure to be implemented, owing to the risk level and the nature of the evaluated operation or process. .

The variables generally used by the various methodologies are:

- Intrinsic hazard of chemical agents
- Frequency / duration of exposure
- Quantity of chemical agent used or present
- Volatility or dust generation of chemical agent
- Method of use
- Type of control

By assigning semiquantitative indices to some of these variables (as these are simplified methodologies, normally not all are selected), the risk can be categorised.

The following are indicated below as an example:

A. a simplified methodology for assessing the risk due to exposure (through inhalation or the skin) to chemical agents
B. a simplified methodology for assessing the risk of an accident resulting from the presence of chemical agents

A. SIMPLIFIED METHODOLOGY FOR ASSESSING THE RISK DUE TO EXPOSURE TO HAZARDOUS CHEMICAL AGENTS

This methodology was developed by the Health & Safety Executive to assess the risk due to exposure to hazardous chemical agents and is called COSHH Essentials.

This methodology is used to determine the control measure appropriate to the operation being assessed and not specifically to determine the existing level of risk. This is its strong point as it provides practical solutions in the form of numerous "control sheets".

We will assume from now on that the control levels obtained through this method correspond to levels of risk. These will be "potential" levels of risk as the existing control measures are not used as an input variable in the method. Having categorised the risk into 4 levels, some general information is given on how to proceed at each level.
The part of the methodology for categorising the risk into the 4 groups[20] is reproduced below. This takes account of three process variables:

a) Intrinsic hazard of the substance
b) Its tendency to pass into the environment
c) The quantity of substance used in each operation

[20] The full method (COSHH Essentials. Health and Safety Executive, 2003) can be consulted at http://www.coshh-essentials.org.uk

a) The *intrinsic hazard of substances*, as indicated in Table A2.1, is classified into five categories, A, B, C, D and E, according to the R phrases which must appear in the product label and in its corresponding safety data sheet.

Table A2.1 Intrinsic hazard of chemical substances through inhalation*

A	**B**	**C**	**D**	**E**
R36 R36/38 R38	R20 R20/21 R20/21/22 R20/22	R23 R23/24 R23/24/25 R23/25	R26 R26/27 R26/27/28 R26/28	Category 3 mutagen, R40
R65 R67	R21 R21/22	R24 R24/25	R27 R27/28	R42 R42/43
All substances not assigned any R phrases corresponding to groups B to E	R22	R25	R28	R45
		R34	Category 3 carcinogen, R40	R46
		R35	R48/23 R48/23/24 R48/23/24/25 R48/23/25 R48/24 R48/24/25 R48/25	R49
		R36/37 R36/37/38	R60 R61 R62 R63 R64	Category 3 mutagen, R68
		R37 R37/38		
		R41		
		R43		
		R48/20 R48/20/21 R48/20/21/22 R48/20/22 R48/21 R48/21/22 R48/22		

**The hazard level increases from A to E*

In addition, some substances can pose risks due to contact with skin or external mucosa. These are the substances which have been assigned the R phrases contained in Table A2.2. When these risks arise immediately after contact (phrase R34 "causes burns" for example), the risk associated with this effect will be assessed as indicated in Section B of this annex.

Table A2.2 Skin risk group (S). Substances which are hazardous in contact with the skin or eyes

R21	R27	R38	R48/24
R20/21	R27/28	R37/38	R48/23/24
R20/21/22	R26/27/28	R41	R48/23/24/25
R21/22	R26/27	R43	R48/24/25
R24	R34	R42/43	R66
R23/24	R35	R48/21	
R23/24/25	R36	R48/20/21	
R24/25	R36/37	R48/20/21/22	
	R36/38	R48/21/22	
	R36/37/38		

When instead of (or in addition to) the above, the HCA gives rise to risks due to contact with the skin in the long term (for example, phrase R48 "Danger of serious damage to health by prolonged exposure"), prevention measures designed to prevent contact between the HCA and the skin or mucosa must be immediately adopted as, in this case, there are no simple assessment systems available at the present time[21].

b) The *tendency to pass into the environment* is classified as high, medium and low and is measured, in the case of liquids, by their volatility and working temperature (Figure A2.1), which define the evaporation capacity of the agent, and in the case of solids, by their tendency to form dust (Table A2.3).

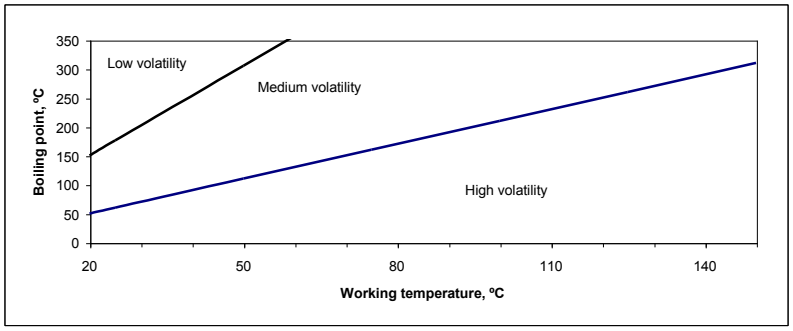


Figure A2.1 Levels of volatility of liquids

[21] The European "Riskofderm" project is developing a tool to assess and manage the risk due to skin exposure. Information may be obtained from *Ann. occup. Hyg.*, Vol. 47, No 8, pp. 629-640, 2003 and at: http://www.iras.uu.nl/research/projects_exp_assess_occ_hyg/ex02.php

Table A2.3 Tendency of solids to form dust*

Low	Medium	High
Substances in the form of pellets that do not tend to break down. No dust production is observed during use. Examples: PVC pellets, waxed flakes, nuggets, etc.	Granular or crystalline solids. When used, dust production is observed which is rapidly deposited and can be seen on adjacent surfaces. Example: detergent powder	Powders: Fine and low density. When used, clouds of dust that remain in the air for several minutes are observed. Examples: cement, carbon black, chalk, etc.

**If in doubt, select the higher category.*

c) The *quantity of substance* used is classified as small, medium or large as indicated in Table A2.4.

Table A2.4 Quantity of substance used (by order of magnitude)

Quantity of substance	Quantity used per operation
Small	Grams or millilitres
Medium	Kilograms or litres
Large	Tonnes or cubic metres

Using these three pieces of information, Table A2.5 indicates the foreseeable level of risk according to the hazard category, the tendency to pass into the environment and the quantity of substance used. Four levels are indicated with each one being linked to a prevention strategy described below which, in all cases, must include the application of the general principles for prevention (Article 5 of the Directive) considered further on in this Guide.

Table A2.5 Determination of the level of risk*

NOTE: AMENDED TABLE !

Hazard level A				
	Volatility / Dust Generation			
Quantity used	*Low Volatility or Dust Generation*	*Medium Volatility*	*Medium Dust Generation*	*High Volatility or Dust Generation*
Small	**1**	**1**	**1**	**1**
Medium	**1**	**1**	**1**	**2**
Large	**1**	**1**	**2**	**2**

Hazard level B				
	Volatility / Dust Generation			
Quantity used	*Low Volatility or Dust Generation*	*Medium Volatility*	*Medium Dust Generation*	*High Volatility or Dust Generation*
Small	**1**	**1**	**1**	**1**
Medium	**1**	**2**	**2**	**2**
Large	**1**	**2**	**3**	**3**

Hazard level C				
	Volatility / Dust Generation			
Quantity used	*Low Volatility or Dust Generation*	*Medium Volatility*	*Medium Dust Generation*	*High Volatility or Dust Generation*
Small	**1**	**2**	**1**	**2**
Medium	**2**	**3**	**3**	**3**
Large	**2**	**4**	**4**	**4**

Hazard level D				
	Volatility / Dust Generation			
Quantity used	*Low Volatility or Dust Generation*	*Medium Volatility*	*Medium Dust Generation*	*High Volatility or Dust Generation*
Small	**2**	**3**	**2**	**3**
Medium	**3**	**4**	**4**	**4**
Large	**3**	**4**	**4**	**4**

Hazard level E
In all situations involving substances of this hazard level, the level of risk will be regarded as 4.

**The levels of risk obtained using this method are 1, 2, 3 or 4.*

Having determined the level of risk, the method offers technical solutions of different types according to the operation being assessed. These control sheets are not reproduced here in full but Chapter 3 of Part I (Specific prevention and protection measures) contains some of these solutions on the reverse of each sheet.
The actions to be taken after categorising the risk can be summarised as follows:
Level of risk 1

In general, in these situations the risk to the health and safety of workers may be regarded as *slight* within the meaning of Article 5(4) of Directive 98/24/EC. If, *in addition*, the application of the general principles for prevention (Chapter 2 of Part I of the Practical Guidelines) is sufficient to reduce this risk, Article 5(4) of the Directive establishes that the provisions of Articles 6, 7 and 10 do not need to be applied.
As a result, these situations will generally not require the effectiveness of the prevention measures to be checked by carrying out environmental measurements, except where this is required by national regulations.

In general, such situations can be controlled through the use of general ventilation.

Level of risk 2

In situations of this type, specific prevention measures to control the risk will have to be used. The type of specific installation most commonly used is local extraction. Specialist suppliers are generally needed to design and build this.

It is important to select suppliers according to their proven experience with this type of installation and also to clearly specify that the aim of the installation is to ensure that the concentration of chemical substances in the workplace is kept as far below the limit value as possible.

Level of risk 3

In situations of this type, closed systems or containment must be used whereby there is no possibility of the chemical substance passing into the atmosphere during ordinary operations. Whenever possible, the process must be maintained at a pressure lower than atmospheric pressure to prevent substances from escaping.

In risk levels 2 and 3, after the implementation of control measures, a detailed quantitative assessment of the exposure should be made, according to the contents of annex 4 (sampling strategy) and annex 5 (sampling and analysis). However, if there are signs that the exposure is clearly lower than occupational limit values, the confirmation of this may be undertaken with less exigent assessment procedures than those mentioned in annex 4.

The result of the quantitative assessment will show the possible need of additional control measures and the possible need of a programme of periodic measurements of the exposure (see annex 4). In any case, the paramenters related to a correct operation of the installations will be periodically checked in order to assure their efficacy along the time.

For levels of risk 2 and 3, a quantitative evaluation of the exposure is recommended, as laid down in Annex 4 to these Practical Guidelines on the sampling strategy, and in Annex 5 on sampling and analysis. In any case, the effectiveness of the prevention measures used must be periodically checked by measuring the substances in the environment. It may also be appropriate to check other characteristics of the system which may indicate whether this is operating correctly (such as the speed at the mouth of an extraction hood). However, these checks will be additional to, and will not replace, the measurement of the environmental concentration in the workplace.

Level of risk 4

Situations of this type are those where either extremely toxic substances are used or substances of moderate toxicity are used in large quantities and where these could easily be released into the atmosphere. If substances regulated by Council Directive 90/394/EEC of 28 June 1990 on the protection of workers from the risks related to exposure to carcinogens at work (Sixth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC) are used, the provisions of this Directive and the national regulations transposing this must also be respected. This Directive has been amended by Directive 97/24/EC and by Directive 1999/38/EC including mutagens in the scope.

In these cases it is essential that measures specifically designed for the process in question are adopted, by seeking the advice of an expert. This level of risk requires the quantitative evaluation of exposure in accordance with the procedures laid down in Annexes 4 and 5 to these Practical Guidelines. The frequency of the periodic check on the effectiveness of the control installations must also be maximised.

B. SIMPLIFIED METHODOLOGY FOR ASSESSING THE RISK OF ACCIDENT, FIRE AND EXPLOSION DUE TO THE PRESENCE OF HAZARDOUS CHEMICAL AGENTS

The methodology for assessing the risk of a chemical accident which is set out below concerns a proposal aimed at helping undertakings working with HCAs, whether or not in the chemical industry, and especially small and medium-sized enterprises, in their task of identifying the hazards and assessing the risks associated with using said products so that prevention can be correctly and objectively planned using the results obtained in this methodology.

This methodology, applied specifically to the risk associated with storing and using hazardous chemical agents, focuses on the predicted damage and not on the maximum damage. It incorporates and develops the experience in applying simplified methodologies based on estimating the probability of occurrence of the hazardous situation analysed, the frequency of exposure to this and the consequences normally expected if this situation does occur. These parameters are used by the W.T. Fine method and by various methods developed by the INSHT (Instituto Nacional de Seguridad e Higiene en el Trabajo – Spanish National Institute for Health and Safety at Work). They are also the criteria used by some harmonised standards produced by the CEN, including EN 1050 and EN 1127-1.

The proposed methodology will allow the magnitude of the existing risks to be quantified and consequently will allow their priority for correction to be rationally determined. It therefore starts with the identification of existing deficiencies in the installations, equipment, processes, tasks, etc. involving HCAs. These deficiencies or non-compliances are related to the R phrases assigned to the various HCAs involved, thus obtaining the objective hazard rating (OHR) for the situation. The level of exposure to the identified hazard rating is then established and, taking into account the predicted magnitude of the consequences (the consequences normally expected must be pre-established by the person applying the methodology), the risk is assessed and the estimated level of risk for the situation assessed is obtained.

This method therefore determines the level of risk as the product of three variables:

$$\mathbf{LR = OHR \times LE \times LC}$$

Where LR: level of risk
OHR: objective hazard rating
LE: level of exposure
LC: level of consequences

The information provided by this method is intended for guidance only, its aim being to help employers to prioritise their prevention actions based on objective criteria and consequently to help them in the planning of prevention. The process for estimating the variables mentioned is described below.

1. Objective hazard rating

The extent of the link predicted between the set of risk factors taken into account and their direct causal relationship with a possible accident is referred to as the objective hazard rating (OHR). The numerical values used in this methodology and their meanings are shown in Table A2.6.

Table A2.6 Determination of the objective hazard rating

OBJECTIVE HAZARD	OHR	MEANING
Acceptable	-	No significant anomalies have been detected. The risk is controlled. Involves taking the measures established for level of risk 1 in Table A2.12.
Improvable	2	Risk factors of minor importance have been detected. The set of existing prevention measures in relation to the risk could be improved.
Deficient	6	Risk factors which need to be corrected have been detected. The set of existing prevention measures in relation to the risk does not guarantee sufficient control of the risk.
Very Deficient	10	Significant risk factors have been detected. The set of existing prevention measures in relation to the risk is ineffective.

It is proposed that a questionnaire (Table A2.7), supplemented by Table A2.8, is used to assess the OHR. Each question in the questionnaire is assigned, depending on the response, to a rating which in some cases is independent of the HCA involved (and is indicated in the questionnaire itself) but which generally depends on the R phrases assigned to the HCA.

Therefore, for example, a negative response to Question 5 will lead to a rating of improvable if the HCA is assigned phrase R21 or to a rating of very deficient if it is assigned any of phrases R1 to R6.

The questionnaire is intended to check the degree of compliance through a number of questions which are presumed to be fundamental when establishing the level of deficiency in installations, equipment, processes, tasks, etc., involving HCAs. It will obviously be necessary to refine its content by replacing or supplementing the questions asked with others meeting the legal or regulatory requirements in individual countries or the situation or needs of the undertaking applying this.

In addition, those questions intended to identify deficiencies where non-compliance may give rise to a fire or explosion (deficient or insufficient control of fuel and sources of ignition) may be separated from the questionnaire. The data obtained from these questions will determine the probability of occurrence which, when assessed together with the degree of compliance with the fire protection measures required by regulation, will provide information on the level of the fire risk. In this way, the assessment of the fire or explosion risk will be clarified and extended.

Therefore, *each question results in a rating* which may be “very deficient”, “deficient” or “improvable” (if the question is applicable) in line with the risk factors present and the intrinsic hazard of the HCA which is known from its R risk phrases. No rating is given for Question 1 which is asked as a “key” question, since a negative response would mean that there were no HCAs in the undertaking and it would therefore not be necessary to continue with the questionnaire.

Depending on all the responses, an *overall rating of the deficiency level* is obtained which may be “very deficient”, “deficient”, “improvable” or “acceptable” according to the following criteria:

a) The overall rating will be “very deficient” if any of the questions are rated as “very deficient” or if more than 50% of the applicable questions receive the rating of “deficient”.

b) The overall rating will be “deficient” if, while not being “very deficient”, any of the questions are rated as “deficient” or if more than 50% of the applicable questions receive the rating of “improvable”.
c) The overall rating will be “improvable” if, while not being “very deficient” or “deficient”, any of the questions are rated as “improvable”.
d) The overall rating will be acceptable in other cases.

Table A2.7 Check questionnaire for identifying accident risk factors due to HCAs*

	YES	NO	Proc No	Negative response implies	Rating
1. Do you store, use, produce, etc. Hazardous Chemical Agents (HCAs) in the form of raw materials, intermediate products, by-products, finished products, waste, cleaning products, etc.				The questionnaire must not be completed	
Identification of chemical agents					
2. Are HCAs present during work, either on a regular basis or occasionally, identified and inventoried.					VERY DEFICIENT
3. Is the original packaging of HCAs correctly labelled.					VERY DEFICIENT
4. Is the above labelling kept when the HCA is transferred to other packaging or containers.					VERY DEFICIENT
5. Have labels identifying the product and direction of flow of liquids been stuck, attached or painted on pipes carrying HCAs.				Go to Table A2.8	
6. Have labels been placed along the pipe in sufficient numbers and in areas of special risk (valves, connections, etc.)					IMPROVABLE
7. Is a safety data sheet (SDS) available for all HCAs which are or may be present during work and, if necessary, is there sufficient and appropriate information on those HCAs without SDSs (waste, intermediate products, etc.)				Go to Table A2.8	
Storage/packaging of chemical agents					
8. Are HCAs stored in special enclosures grouped by risk category and adequately isolated (by distance or by partition) from incompatible agents or agents that may give rise to hazardous reactions.				Go to Table A2.8	
9. Is the storage area properly ventilated by either natural or forced draught.					DEFICIENT
10. When required due to the product quantity and/or hazard, is the collection and removal of liquid HCA leaks or spillages to a safe container or area ensured in storage, use and/or production areas.					DEFICIENT
11. Is the presence or use of "uncontrolled" ignition sources in flammable HCA stores banned and is compliance with this ban exhaustively monitored and assured.				Go to Table A2.8	
12. Does packaging containing HCAs offer sufficient physical or chemical resistance and is it free of any signs of impacts, cuts or deformations.				Go to Table A2.8	
13. Is packaging containing HCAs totally secure (automatic closure, safety closure with interlock, double wrapping, shock absorbent coating, etc.)				Go to Table A2.8	
14. Is packaging transported, whether by manual or mechanical means, using equipment and/or implements that ensure that this is stable and properly secured.				Go to Table A2.8	

	YES	NO	Proc No	Negative response implies	Rating
Chemical agent use/process					
15. Is only the quantity of HCA strictly necessary for the immediate work kept in the workplace (never quantities greater than those needed for the shift or working day).					IMPROVABLE
16. Are HCAs present in the workplace for use during the shift or working day and those not currently in use stored in appropriate containers, protected cabinets or special enclosures.					IMPROVABLE
17. Is the transfer of HCAs by open pouring avoided.				Go to Table A2.8	
18. Is the creation and/or accumulation of static discharges during the transfer of flammable liquids rigorously monitored.				Go to Table A2.8	
19. Is the electrical installation in areas with a risk of flammable atmospheres explosion-proof and are ignition sources of any kind also monitored [+].				Go to Table A2.8	
20. Is the electrical installation of corrosive product equipment, instruments, rooms and stores adequate.				Go to Table A2.8	
21. Are the characteristics of materials, equipment and tools appropriate for the nature of the HCAs used.				Go to Table A2.8	
22. Is the absence of leaks and, in general, the correct state of installations and/or equipment checked before use.				Go to Table A2.8	
23. Do equipment or processes requiring this have systems to detect unsafe conditions (LIL level in drying tunnel, reactor temperature/pressure, fill level of a tank, etc.) associated with an alarm system.				Go to Table A2.8	
24. Do existing detection systems act to shut down the process when required by critical situations.					DEFICIENT
25. Are vents and outlets of safety devices for flammable/explosive products channelled to a safe place and equipped with flares where required.				Go to Table A2.8	
26. Are devices available for the safe treatment, absorption, destruction and/or containment of effluent from safety devices and vents.				Go to Table A2.8	
27. Are operations that involve the possible release of HCA gas, vapour, dust, etc. carried out using closed processes or, failing this, in well-ventilated areas or in installations with local extraction systems.				Go to Table A2.8	
28. In general, have the collective protection measures needed to isolate HCAs and/or limit exposure and/or contact by workers been implemented.				Go to Table A2.8	
Organisation of prevention in the use of chemical agents					
29. Is work authorisation required when carrying out operations involving a risk on containers, equipment or installations containing or which have contained HCAs.				Go to Table A2.8	
30. Is the control of access by external or unauthorised personnel to areas where HCAs are stored, loaded/unloaded or processed guaranteed.				Go to Table A2.8	

	YES	NO	Proc No	Negative response implies	Rating
31. Have workers been properly informed about the risks associated with HCAs and correctly trained in the prevention and protection measures to be adopted.				Go to Table A2.8	
32. Do workers have access to the SDS provided by the supplier.					IMPROVABLE
33. Are written work procedures available for the performance of tasks involving HCAs.				Go to Table A2.8	
34. Is there a preventive maintenance programme and also a predictive maintenance programme for equipment or installations whose correct operation is crucial to process safety.					DEFICIENT
35. Is the cleanliness of workplaces and work posts ensured. (Has a programme been set up and is its application monitored).					IMPROVABLE
36. Are specific means available for neutralising and cleaning up spillages and/or for controlling leaks and do action instructions exist.					DEFICIENT
37. Is there a waste management plan and is its application monitored.					DEFICIENT
38. Have correct personal hygiene rules been implemented (hand washing, changing of clothes, ban on eating, drinking or smoking at work posts, etc) and is their application monitored.					IMPROVABLE
39. Is an Emergency Plan available for critical situations in which HCAs are involved (leaks, spillages, fire, explosion, etc.)					VERY DEFICIENT
40. In general, have the organisational measures required in order to isolate HCAs and/or limit exposure and/or contact by workers with these been implemented.				Go to Table A2.8	
Use of PPE and emergency installations					
41. Is the necessary personal protective equipment (PPE) available and is its effective use monitored in the various tasks at risk of exposure to, or contact with, HCAs.				Go to Table A2.8	
42. Are decontaminating showers and eyebath fountains available close to places where HCA splashes are possible.				Go to Table A2.8	
43. In general, is PPE and work clothing correctly managed.					DEFICIENT
44. Have any other deficiencies or shortcomings been detected with regard to collective protection, organisational measures and use of PPE: Describe and assess.					

[*] *Open questionnaire proposed as a guide; under no circumstances should this be regarded as exhaustive and closed.*

[+] *To determine whether there is a risk of an explosive atmosphere, the work area should firstly be classified according to the presence of flammable substances and, where applicable, this should be checked using an explosion meter.*

Table A2.8 Assessment criteria

Question nº	VERY DEFICIENT	DEFICIENT	IMPROVABLE
5,7 8	R1 to R6, R7, R12, R14, R15, R16, R17, R19, R27, R28, R35, R39	R8, R9, R11, R18, R24, R25, R30, R34, R37, R41, R44	R10, R21, R22, R36, R38
11	R1 to R6, R7, R12, R14, R15, R16, R17, R19	R8, R9, R11, R18, R30, R44	R10
12,13,14	R1 to R6, R7,R12, R17,R19,R27,R35,R39	R9, R11, R24, R34, R37, R41	R10,R21,R36,R38
17	R7,R12,R17,R27,R35,R39	R11,R18,R24,R30,R34, R37,R41	R10, R21,R36
18	R7, 12	R11,R18,R30	R10
19	R1 to R6, R12, R15	R8, R11, R18, R30	
20	R35	R34	
21,22,23	R1 to R6, R7, R12, R14, R15, R16, R17, R19, R27,R35, R39	R8, R9, R11, R18, R24,R30, R34, R37, R41, R44	R10, R21, R36, R38
24		R1 to R6, R7, R12, R14, R15, R16, R17, R19, R27,R35, R39	R8, R9,R10, R11, R18,R21, R24, R30,R34,R36,R37,R38,R41, R44
25	R2,R3,R5,R6,R7,R12, R14, R15,R16, R17,R19	R8,R9,R11,R18,R30, R44	R10
26	R27,R35,R39	R24,R34,R37,R41	R21,R36,R38
27	R7,R12,R27,R35,R39	R11,R18,R24,R30,R34,R37,R41	R10, R21,R36
28	R1 to R6, R7, R12, R14, R15, R16, R17, R19, R27, R28, R35, R39	R8, R9, R11, R18, R24, R25, R30, R34, R37, R41, R44	R10, R21, R22, R36, R38
29			R10
30, 31	R1 to R6, R7, R12, R14, R15, R16, R17, R19, R27, R28, R35, R39	R8, R9, R11, R18, R24, R25, R30, R34, R37, R41, R44	R10, R21, R22, R36, R38
33			R10
40	R8, R9, R11, R18, R24, R25, R30, R34, R37, R41, R44	R8, R9, R11, R18, R24, R25, R30, R34, R37, R41, R44	R10, R21, R22, R36, R38
41,42	R27, R35, R39	R24, R34, R39,R41	R21,R36

2. Level of exposure

The level of exposure (LE) is an indicator of the frequency with which exposure to the risk occurs. The level of exposure can be estimated according to the time spent in areas and/or tasks where the risk has been identified. Its meaning is shown in Table A2.9.

Table A2.9 Determination of the level of exposure

LE	MEANING
1	Occasionally.
2	Sometimes during the working day and for short periods of time.
3	Several times during the working day for short periods of time.
4	Continuously. Several times during the working day for prolonged periods of time.

As can be seen from Table A2.6, the values assigned are lower than those assigned for the objective hazard rating given that, if the risk situation is controlled, high exposure should not give rise to the same level of risk as a very deficient situation involving low exposure.

3. Level of consequences

The consequences normally expected if the risk should occur will be taken into consideration. Four levels of consequences (LC) which categorise the personal harm which can be expected should the risk occur are established.

As can be seen from Table A2.10, the numerical value assigned to the consequences is much higher than those of the objective hazard rating and level of exposure, given that the consequences should always be much more heavily weighted in the risk assessment.

Table A2.10 Determination of the level of consequences

LC	MEANING
100	One or more fatalities
60	Serious injuries which may be irreversible
25	Normally reversible injuries
10	Minor injuries

LC	MEANING
10	Minor injuries
25	Normally reversible injuries
60	Serious injuries which may be

	irreversible
100	One or more fatalities

4. Level of risk

All the steps carried out up to this point lead to the determination of the level of risk which is obtained by multiplying the objective hazard rating by the level of exposure and the level of consequences (Table A2.11).

Table A2.11 Determination of the level of risk

		(OHR x LE)			
		2 - 4	**6 - 8**	**10 - 20**	**24 – 40**
(LC)	**10**	20 – 40	60 – 80	100 – 200	240 - 400
	25	50 - 100	150 – 200	250 – 500	600 - 1000
	60	120 – 240	360 – 480	600 – 1200	1440 - 2400
	100	200 – 400	600 – 800	1000 – 2000	2400 - 4000

Table A2.12 gives the meanings of the four levels of risk obtained.

Table A2.12 Meanings of the various levels of risk

LEVEL OF RISK	**LR**	**MEANING**
1	40 - 20	Improve as much as possible. Periodic checks are required to ensure that the effectiveness of current measures is maintained.
2	120 - 50	Establish measures to reduce the risk and introduce these within a specified period
3	500 - 150	Correct and adopt short-term control measures
4	4000 - 600	Situation requiring urgent correction

ANNEX 3

APPLICATION EXAMPLES OF THE PRINCIPLES FOR PREVENTION AND SPECIFIC MEASURES IN TWO INDUSTRIAL PROCESSES

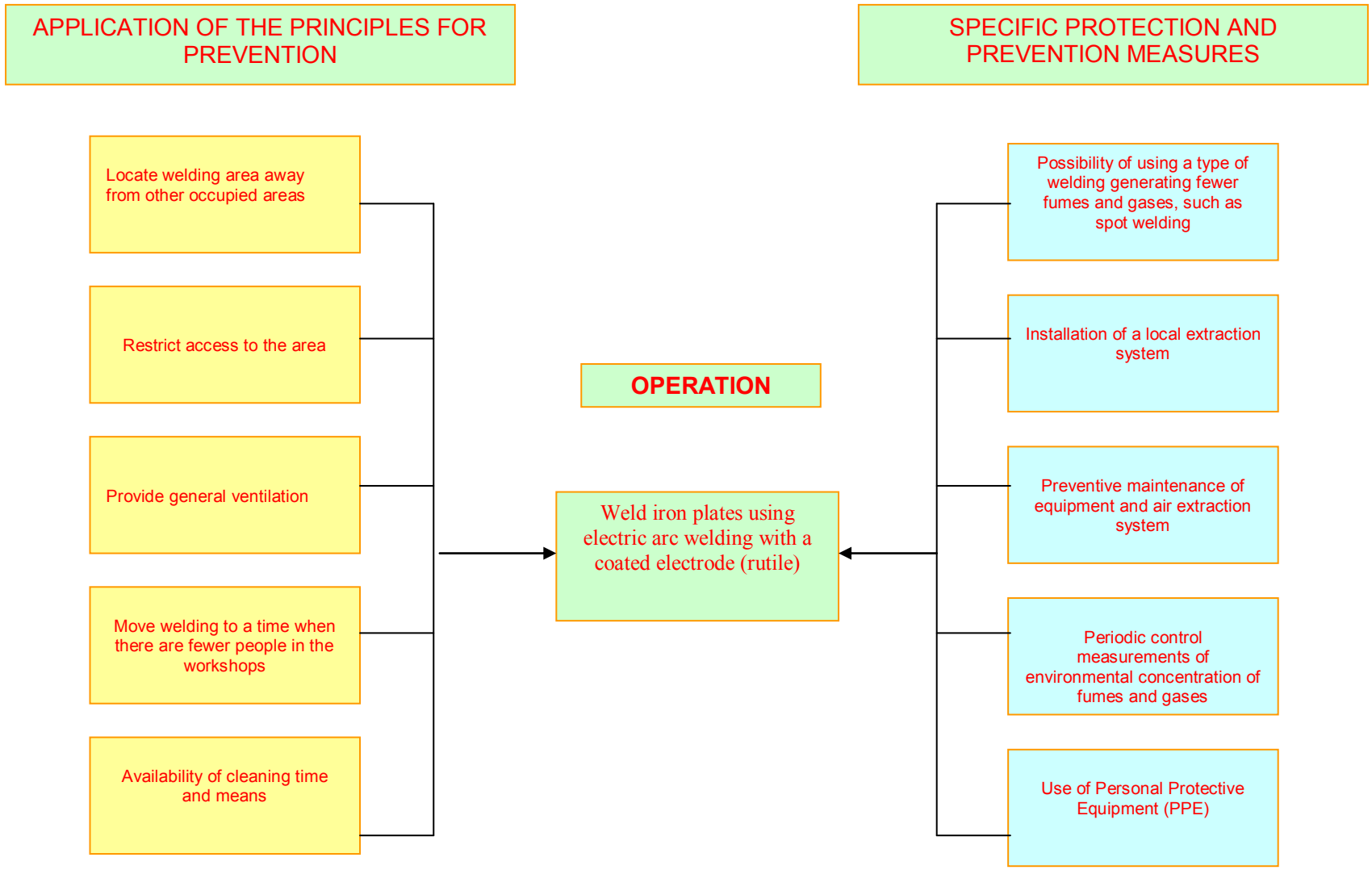
A) APPLICATION IN AN OPERATION FOR THE ELECTRIC ARC WELDING OF IRON PLATES WITH RUTILE-COATED ELECTRODES

This operation generates metal oxide fumes from the electrode, such as titanium dioxide, and from the base metal, such as iron oxide. These are termed *welding fumes* and inhaling them can lead to irritation of the respiratory tract and to pneumoconiotic-type effects. In addition, gases such as carbon monoxide and dioxide (asphyxiants), nitrogen dioxide and ozone (lung tissue irritants) are formed. The latter is generated by the action of ultraviolet radiation, emitted in the electric arc, on oxygen atoms in the air.

The generation of fumes and gases increases as the density of the electric current used in the welding increases. Moreover, if the items to be welded contain residues of oil or a degreaser, other chemical agents, such as acrolein and phosgene, which are also lung tissue irritants, may be generated.

Table A3.1 shows the preventive actions to be taken on applying the general principles and specific measures appropriate to an operation such as that described.

Table A3.1 General principles for prevention and specific prevention measures. Welding operation application example



B) APPLICATION IN AN OPERATION INVOLVING PAINTING ITEMS BY SPRAY PAINTING AND DRYING OF THE SOLVENT

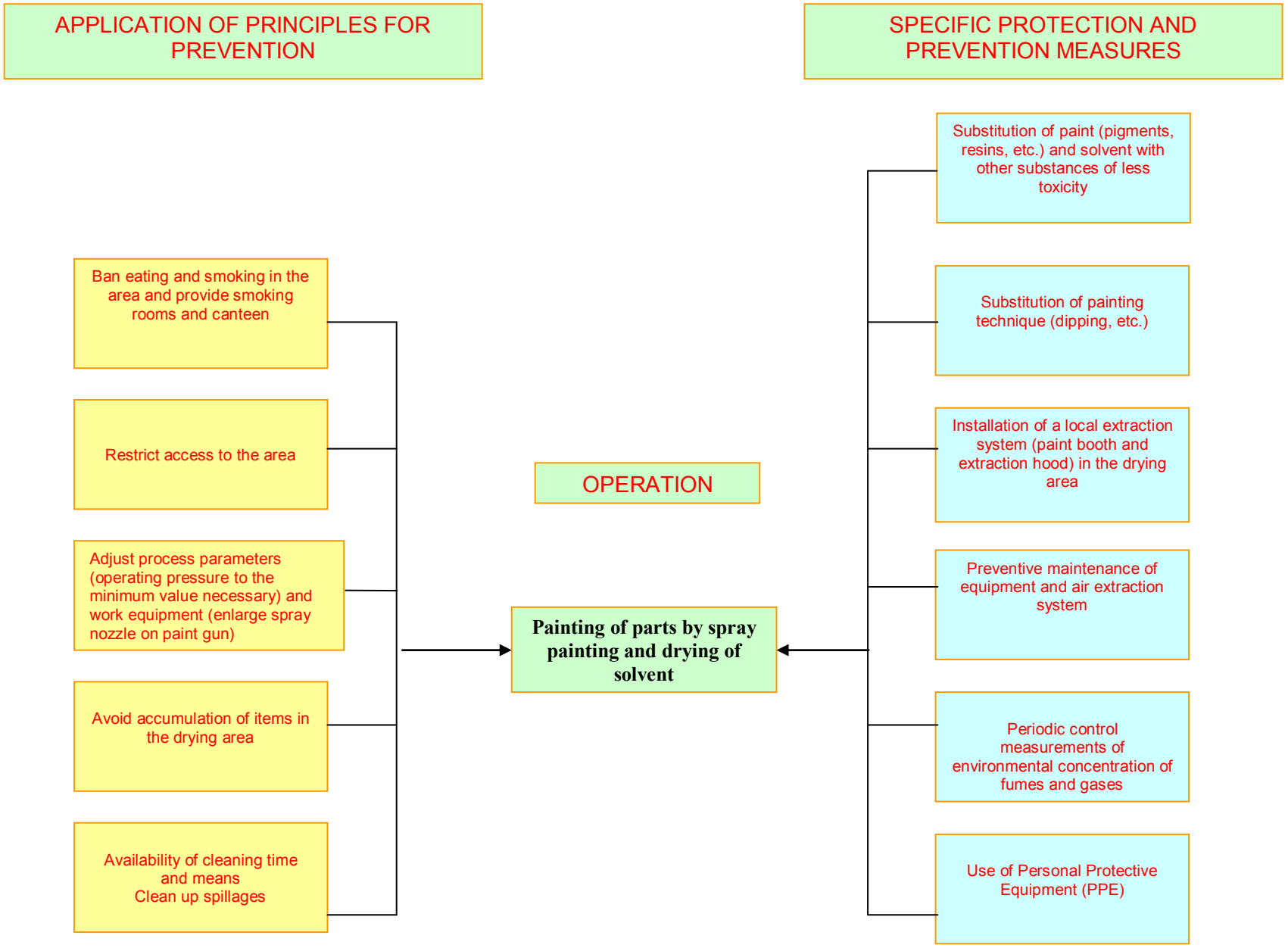
Spray painting consists of using compressed air to propel paint spray onto the item to be painted. The paint is directed using a manually-operated tool called a *gun*. The paint dries after a period of time during which the solvent, made up of highly volatile substances, evaporates. Evaporation of the solvent leads to the formation of vapours, such as toluene, which is one of the most widely used. These vapours are in general toxic to the central nervous system and irritant to the respiratory tract and are liver toxins.

Moreover, the pigments and other components of the paint (resin) are projected at high speed onto the item which is why, due to their inertia, many particles rebound on the item and return to the painter's breathing area. The pigments, which give colour to the paint, are often the most toxic of the substances, such as chromium or lead oxides.

Paint spraying generates aerosols and vapours depending on the pressure exerted on the gun. The ambient temperature affects the rate of evaporation of the solvent.

Table A3.2 shows the preventive actions to be taken on applying the general principles and specific measures appropriate to an operation such as that described.

Table A3.2 General principles for prevention and specific prevention measures. Painting operation application example



ANNEX 4

QUANTITATIVE EVALUATION OF EXPOSURE TO CHEMICAL AGENTS

CONTENTS

1. RISK ASSESSMENT AND EVALUATION OF EXPOSURE

Assessing the risk due to exposure[22] to chemical agents is intended to achieve the same three objectives as for any other type of risk, i.e.:

1. To decide whether or not further prevention measures need to be adopted in addition to those already in place.
2. To determine the type of prevention measures that should be adopted.
3. To prioritise the prevention measures required.

Moreover, provided that there are no insuperable practical difficulties and that the conclusion is not completely obvious right from the outset, risk assessment should be based on a quantitative evaluation of exposure. Adopting this approach may lead to less error than with a direct consideration of the material and organisational risk factors giving rise to the exposure. This method of action is characteristic of Industrial Hygiene and constitutes its specific technical content.

However, evaluating exposure to a chemical agent only provides an estimate of (or rather, an opinion on) the probability of that chemical agent having its characteristic effect. It does not provide any information on the seriousness of that effect. Since this parameter must be taken into account in order to assess the risk, the exposure evaluation will only be part of the process.

Therefore, it should not be forgotten that, once the evaluation of all the relevant exposures has been completed, the intrinsic hazards posed by the various chemical agents will still need to be considered, before deciding on an order of preference for the respective prevention measures. Only if all exposures involve the same chemical will the hierarchy of exposures be a faithful reflection of the hierarchy of the corresponding risks.

2. QUANTITATIVE EVALUATION OF EXPOSURE TO CHEMICAL AGENTS

2.1. INDICATIONS

The exposure evaluation procedure described in the following sections complements rather than replaces the simplified methodology discussed in point 1.2.2 of this document. It should be applied, therefore, in cases in which said methodology indicates a need for environmental measurements (all cases other than those of level of risk 1) and at the points of the process specified therein.

In summary, measurement is an option to be justified rather than a routine but, when indicated, it must comply with a standardised procedure that ensures a minimum level of reliability and validity of its results.

[22] In this text, as is usually the case, the term “exposure”, where not qualified, should be understood to mean “by inhalation”.

2.2. HOMOGENEOUS EXPOSURE GROUPS (HEG)

A homogeneous exposure group is defined as the association of a job and a chemical agent (or several that produce the same effect) in a given environment[23].

Thus, in principle, among workers who do the same job[24], there will be as many HEGs as there are chemical agents with independent effects to which they are exposed.

The whole exposure evaluation procedure described in this annex, and therefore also its conclusions, applies to each homogeneous exposure group.

Of course, the most useful aspect of this concept is that it allows conclusions to be drawn about the group based on measurements made for only some of its members. EN 689:1995[25] allows a proportion as low as one in ten.

2.3. CLASSIFICATION OF EXPOSURES

The conclusion of the quantitative evaluation process will be the classification of the exposure of any HEG into one of the three following categories:

***Acceptable exposure**:* Does not require monitoring by periodic measurements.

***Tolerable exposure**:* Poses a risk of deviation, so therefore requires monitoring by periodic measurements.

***Unacceptable exposure**:* Requires correction to reduce exposure, followed by another evaluation.

3. INITIAL EVALUATION

If the aim is to measure workers' real exposure, concentration measurements must be personalised, i.e. made using equipment worn by the subjects while they work, with the sampling head located in the breathing area[26].

Area measurements, i.e. those made at fixed positions, can sometimes be used to evaluate excessive exposure, so should not be completely dismissed.

3.1 EVALUATING DAILY EXPOSURE (DE)

DE is the mean concentration of the chemical agent in the worker's breathing area measured, or calculated on a time-weighted basis, over the real working day and applied to a standard eight-hour day. Applying the mean concentration to this standard working day means regarding the whole set of the worker's different exposures throughout the real working day, each with its corresponding duration, as being equivalent to a single uniform eight-hour exposure.

[23] Definition taken from the Rhodia document referred to in Part IV (Bibliography).
[24] A job is defined as the performance of a function in a specific environment.
[25] See reference in Part IV (Bibliography).
[26] See definition in EN 1540 Workplace atmospheres. Terminology.

It is obvious that the DE to a chemical agent can only be evaluated when a limit value for this has been defined. Accordingly, the procedure must start with determining one or more DE values in the HEG which is why the first step must be to establish how the DE for a working day is determined.

3.1.1 Determining the DE of a working day

This determination is performed through a three-stage process.

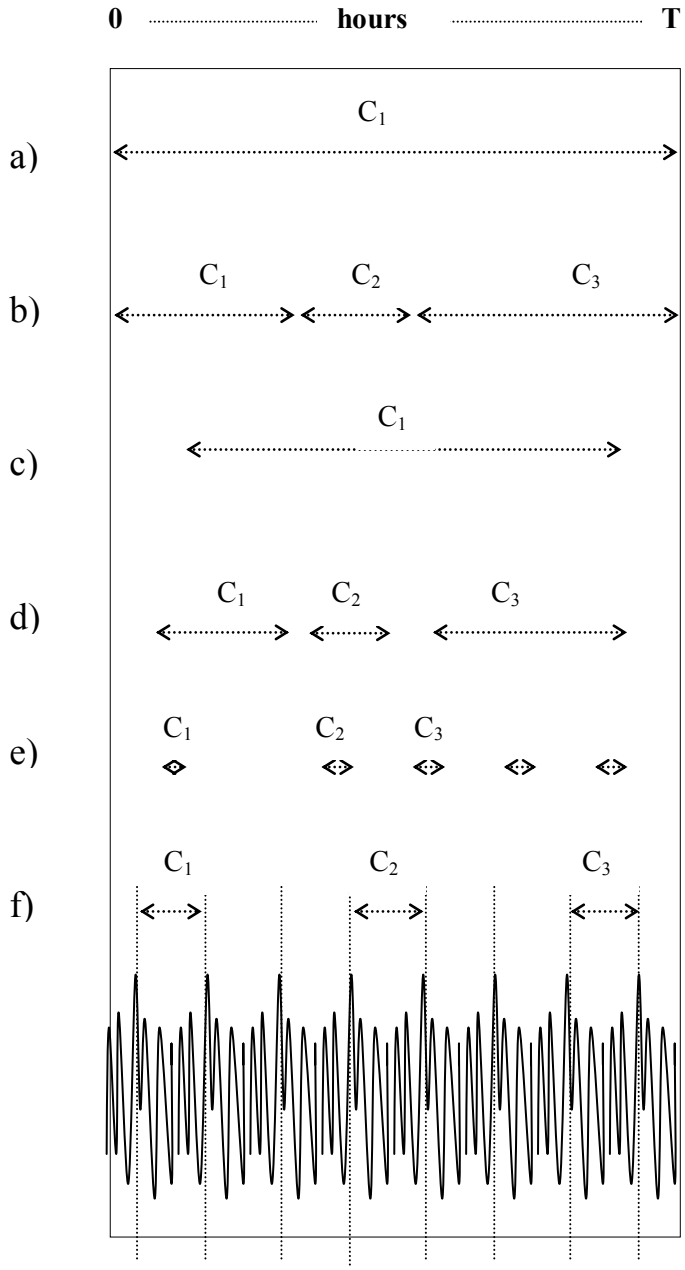
1) Divide the working day into uniform exposure periods.
As the heading suggests, this consists of dividing the working day of the HEG into well-defined tasks in which the exposure can be regarded as uniform[27]. In this way, the concentration will be subject to systematic variations between periods and merely random variations within each one.
This first phase is not essential if a decision is made to measure the whole working day. However, it is advisable even then (unless there are other reasons for taking a single sample) since it provides more information.

2) Sample and calculate the mean concentration for each uniform exposure period.
The next step is to decide on the type of sampling to be used to measure the concentration in each uniform exposure period. The possible strategies (Table A4.1) are:

a) Full period – single sample
b) Full period – consecutive samples
c) Partial period – single sample
d) Partial period – consecutive samples
e) Random point sampling
f) Sampling cycles

[27] The division should be reconsidered if sample concentrations within a period are subsequently found (if the sampling method permits this) to be less than half or more than double the mean for the period.

Table A4.1 Sampling strategies



The following points should be noted about these different methods:

- The two full-period methods (a and b) are unquestionably preferable to those based on a partial period. The latter are bound to entail some error which cannot be estimated. In any case, Annex A to EN 689:1995 states that sampling should encompass at least 25% of the represented period.
- With random point sampling, each sample is taken over the shortest time compatible with the measurement method, the samples are all of the same duration and they are taken at times picked at random from the whole represented period. This is the method that gives the largest margin of error in estimating the mean for the period.

- "Sampling cycles" are also random in nature, but each sample necessarily encompasses a complete cycle or a whole number of cycles. This method is therefore restricted to periods in which exposure is of a cyclical nature, so it is not an option in all cases.

Based on the sample concentrations, the mean concentration for the uniform exposure period (C) is obtained from the various strategies by using the following expressions:

a) Full period – single sample

$C = c$

Where c is the single sample concentration.

b) Full period – consecutive samples

$C = \Sigma\ ci\ ti / T$

Where ci is the sample concentrations, ti the durations of the respective samples and T the total period which will of course be equivalent to Σ ti.

c) Partial period – single sample

$C = c$

Where c is the single sample concentration.

d) Partial period – consecutive samples

$C = \Sigma\ ci\ ti / \Sigma\ ti$

Where ci is the sample concentrations and ti the durations of the respective samples.

e) Random point sampling

$C = \Sigma\ ci / n$

Where ci is the sample concentrations and n is the number of samples.

f) Sampling cycles

$C = \Sigma\ ci / n$

Where ci is the sample concentrations and n is the number of samples.

3) Calculate the DE of the working day

This is obtained from the mean concentrations for the uniform exposure periods (C_i) and the respective durations of the latter in hours (T_i), using the following formula:

$$DE = \Sigma\ C_i\ T_i / 8$$

3.1.2. Evaluating the long-term DE

It is known that the DE of an HEG is not constant over time, but varies from day to day even when no systematic differences are apparent in terms of working conditions. In general, based on theoretical considerations and empirical evidence, it is accepted that the DE behaves as a random variable with a lognormal distribution.

Therefore, evaluating the DE of a working day is only of interest to an official inspection body verifying compliance with the regulations on a specific occasion. For employers, who have to rely on the risk assessment to plan their preventive action, only a long-term evaluation, capable of providing a reliable prediction, is of any value.

The two procedures for evaluating the long-term DE set out in the annexes to EN 689 are described below. In both cases, their application requires there to be no systematic day-to-day differences in the working conditions. If such differences exist, however, it is still possible to apply these procedures to the set of least favourable working days, using an excessive exposure evaluation strategy.

3.1.2.1. Based, initially, on a single DE value

The main advantage of this method is that it minimises the number of measurements at the outset, with these being gradually increased as necessary, depending on earlier results[28]. Its main disadvantage is that it does not allow the DE distribution to be characterised by estimating its parameters.

If, depending on the composition of the HEG, the exposure of more than one worker needs to be measured, the procedure should be applied to each one separately and the decision made for the whole group on the basis of the least favourable case.

The procedure is as follows:

1. Obtain a DE value

2. Calculate the relative DE (DE_r) by dividing DE by the relevant limit value (LV-DE)

DE_r = DE / LV-DE

3. If $DE_r \leq 0.1$, *acceptable exposure*

If $DE_r > 1$, *unacceptable exposure*

If $0.1 < DE_r \leq 1$, determine at least two new values for DE_r [29]

4. If DE_{r1} and DE_{r2} and …$DE_{rn} \leq 0.25$, *acceptable exposure*

5. If DE_{r1} or DE_{r2} or…$DE_{rn} > 1$, *unacceptable exposure*

6. If any $DE_r > 0.25$ but all ≤ 1 and GM[30] ≤ 0.5, *tolerable exposure*

7. If GM > 0.5, the options are as follows:

- Improve exposure control and repeat the evaluation procedure
- Obtain new values for DE_r and follow the procedure from step 4, until a conclusion is reached

3.1.2.2. Based on six or more DE values

The graphical procedure for this evaluation is described in Annex G to EN 689:1995.
Only the analytical version[31], not included in the standard, will be presented here, using a number of approximations from the NIOSH Sampling Strategy Manual[32]. The process is as follows:

[28] This makes it easier to use in the case of relatively unstable work processes, in which it can be difficult to predict in advance whether the desired conditions will occur on a specific day.
[29] Corresponding to two further working days, preferably non-consecutive and picked at random.
[30] Geometric mean of DE_r values.

1. Obtain at least 6 DE values, randomly, within the HEG.

2. Check the homogeneity[33] of exposure within the HEG.

3. Transform the DE values into DE_r values, by dividing them by the corresponding limit value (LV-DE).

$DE_r = DE / LV\text{-}DE$

4. Calculate the Napierian logarithms of the DE_r values

$y_i = \ln DE_{ri}$

5. Calculate the sample mean (Y) and the quasi-standard deviation for the sample ($S_{n-1, y}$), using the following formulae:

$Y = \Sigma y_i / n$

$S_{n-1, y} = \sqrt{\Sigma (y_i - Y)^2 / n - 1}$

6. Standardise the transform of the limit value, ln (LV-DE / LV-DE), by calculating the statistic:

Z[34] $= (0 - Y) / S_{n-1, y}$

7. Look up in the standardised normal distribution table (Table A4.1) the probability (p) of exceeding the calculated Z value. This is the probability that the DE for any one working day will exceed the limit value.

If $p \leq 0.1\%$, *Acceptable exposure*. Green status.

If $p > 5\%$, *Unacceptable exposure*. Red status.

If $0.1\% < p \leq 5\%$, *Tolerable exposure*. Orange status.

3.2 EVALUATING SHORT-TERM EXPOSURE (SE)

SE is defined as the mean concentration in any 15-minute period in the working day. In contrast to the DE, for which there can only be one value per working day, HEG and chemical agent, there can be as many SE values as there are 15-minute periods in the working day. If overlaps are permitted, this number is virtually infinite.

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[31] The main disadvantage compared with the graphical method is that no check is made as to whether the empirical distribution fits the lognormal model.

[32] Leidel, Busch and Lynch: Occupational Exposure Sampling Strategy Manual. NIOSH, 1977.

[33] If the DE of any worker is less than half or more than double the arithmetic mean for the group, the classification of the subjects should be reassessed.

[34] In fact, this statistic is not Z but t, since the denominator contains not the standard deviation of the population but its sample estimator. However, assuming a normal distribution according to the NIOSH Manual is regarded as an adequate approximation.

If the chemical agent in question has been assigned an SE limit value (LV-SE), which will be the case whenever this evaluation has to be performed, the objective is to ensure that no short-term exposure exceeds this. The first step is therefore to determine the maximum SE of the working day.

3.2.1 Determining the maximum SE

The 15-minute period(s) suspected of causing maximum exposure must be selected systematically, i.e. by analysing the tasks and the circumstances in which these are performed to reveal the most unfavourable.

If the number of periods selected in this way is reasonable, the SE of each is measured and the highest value obtained becomes the maximum SE value sought.

If, on the other hand, the number is very high, a sample of periods to be measured will have to be picked from them at random. Again, the highest SE obtained will be used for the evaluation in the first instance, but, unlike the earlier case, there is no guarantee of having determined the maximum SE.

3.2.2 Evaluating the SE

The procedure can be summarised in the following steps:

1. The maximum measured SE value is compared with the LV-SE.

- If it exceeds this, the evaluation ends with the conclusion that the exposure is *unacceptable*.

- If it does not exceed this, and the measurement periods were selected on a purely systematic basis, the process also ends with the conclusion that the exposure is *tolerable* (max SE > 0.5 LV-SE) or *acceptable* (max SE ≤ 0.5 LV-SE).

- If it does not exceed this, but a random element was involved in selecting the periods, the evaluation procedure must continue in order to estimate the probability of the limit value being exceeded in the whole set of unmeasured suspect periods.

To this end, the widely-accepted initial assumption, also used in the long-term DE evaluation, is that, when there are no systematic differences between periods, SE behaves as a random variable with a lognormal distribution. So, from a random sample of SE values, as here, it is possible to estimate the distribution parameters and, on that basis, arrive at the probability value sought. The procedure, largely analogous to that described in 3.1.2.2., continues as follows:

2. Transform the measured SE values into SE_r values, by dividing them by LV-SE.

3. Calculate the Napierian logarithms of the SE_r values

$$y_i = \ln SE_{ri}$$

4. Calculate the sample mean (Y) and the quasi-standard deviation for the sample ($S_{n-1, y}$), these being the best estimates of the population mean and standard deviation, using the following formulae:

$$Y = \Sigma\, y_i / n$$

$$S_{n-1, y} = \sqrt{\Sigma\, (y_i - Y)^2 / n - 1}$$

5. Standardise the transform of the limit value, ln (LV-SE / LV-SE), by calculating the statistic:

$$Z = (0 - Y) / S_{n-1, y}$$

6. Look up in the standardised normal distribution table (Table A4.1) the probability (p) of exceeding the Z value obtained. Since p is the probability of any one of the unmeasured periods exceeding the limit value, 1 – p will be the probability that it does not exceed this and $p' = (1 - p)^{k-i}$, where k is the total number of suspect periods and i the number of measured periods, will be the probability of its not being exceeded in any of the unmeasured periods.

7. If p' > 0.9 (90%), exposure is *acceptable*.

If p' < 0.1 (10%), exposure is *unacceptable*.

If 0.1 ≤ p' ≤ 0.9, exposure is regarded as only *tolerable*.

4. PERIODIC EXPOSURE MEASUREMENTS

"Periodic measurements" is the term used to describe a method of exposure monitoring instituted when the results of the initial evaluation do not allow the exposure to be classified as either acceptable or unacceptable and the introduction of additional control measures to achieve acceptable status is not considered justified. The starting point is thus tolerable exposure, since there is no evidence of the limit value having been exceeded, but there is a risk of deviation.

Periodic measurements are not successive evaluations of exposure, so the procedures described above should not be used. Nor should they be confused with the monitoring of risk control measures, such as, for example, periodic checks on ventilation systems, which must always be performed, whether or not periodic exposure measurements need to be made.

Periodic measurements must achieve two objectives:

a) To establish the exposure trend so that corrective measures can be applied, if necessary, before the limit value is exceeded.
b) To adjust the measurement frequency in a flexible fashion to the actual exposure.

In order to do this, periodic measurements must comply with a programme, established from the outset, clearly defining what, where or who to measure, when, how and how often. In this way, the results obtained over time will be comparable with each other and differences between them will only reflect variations in exposure, rather than different measurement criteria.

The moving weighted average method, presented in Annex G to EN 689, can be used to analyse exposure trends from periodic measurement data.

In addition, Annexes D and F to the same standard include two systems for establishing the frequency of measurement. The simpler of the two is presented below. The initial frequency is set at 16 weeks, with the following variation criteria:

1. If the result of a measurement is such that exposure is less than or equal to 25% of the limit value, the next measurement shall be made after 64 weeks.

2. If the result of the measurement is such that exposure is between 25 and 50% of the limit value, the next measurement shall be made after 32 weeks.

3. If the result of the measurement is such that exposure is between 50 and 100% of the limit value, the next measurement shall be made after 16 weeks.

4. If several successive measurements give exposure values of less than 10% of the limit value, the need for any periodic measurement programme at all can be reassessed.

5. If any measurement indicates exposure above the limit value, the necessary preventive measures must be applied and the initial evaluation must subsequently be repeated, using one of the established procedures.

Table A4.1 Standardised normal distribution

Z	p	Z	P	Z	p	Z	p	Z	p	Z	p	Z	p
3.49	0.9998	2.99	0.9986	2.49	0.9936	1.99	0.9767	1.49	0.9319	0.99	0.8389	0.49	0.6879
3.48	0.9997	2.98	0.9986	2.48	0.9934	1.98	0.9761	1.48	0.9306	0.98	0.8365	0.48	0.6844
3.47	0.9997	2.97	0.9985	2.47	0.9932	1.97	0.9756	1.47	0.9292	0.97	0.8340	0.47	0.6808
3.46	0.9997	2.96	0.9985	2.46	0.9931	1.96	0.9750	1.46	0.9279	0.96	0.8315	0.46	0.6772
3.45	0.9997	2.95	0.9984	2.45	0.9929	1.95	0.9744	1.45	0.9265	0.95	0.8289	0.45	0.6736
3.44	0.9997	2.94	0.9984	2.44	0.9927	1.94	0.9738	1.44	0.9251	0.94	0.8264	0.44	0.6700
3.43	0.9997	2.93	0.9983	2.43	0.9925	1.93	0.9732	1.43	0.9236	0.93	0.8238	0.43	0.6664
3.42	0.9997	2.92	0.9982	2.42	0.9922	1.92	0.9726	1.42	0.9222	0.92	0.8212	0.42	0.6628
3.41	0.9997	2.91	0.9982	2.41	0.9920	1.91	0.9719	1.41	0.9207	0.91	0.8186	0.41	0.6591
3.4	0.9997	2.9	0.9981	2.4	0.9918	1.9	0.9713	1.4	0.9192	0.9	0.8159	0.4	0.6554
3.39	0.9997	2.89	0.9981	2.39	0.9916	1.89	0.9706	1.39	0.9177	0.89	0.8133	0.39	0.6517
3.38	0.9996	2.88	0.9980	2.38	0.9913	1.88	0.9699	1.38	0.9162	0.88	0.8106	0.38	0.6480
3.37	0.9996	2.87	0.9979	2.37	0.9911	1.87	0.9693	1.37	0.9147	0.87	0.8078	0.37	0.6443
3.36	0.9996	2.86	0.9979	2.36	0.9909	1.86	0.9686	1.36	0.9131	0.86	0.8051	0.36	0.6406
3.35	0.9996	2.85	0.9978	2.35	0.9906	1.85	0.9678	1.35	0.9115	0.85	0.8023	0.35	0.6368
3.34	0.9996	2.84	0.9977	2.34	0.9904	1.84	0.9671	1.34	0.9099	0.84	0.7995	0.34	0.6331
3.33	0.9996	2.83	0.9977	2.33	0.9901	1.83	0.9664	1.33	0.9082	0.83	0.7967	0.33	0.6293
3.32	0.9995	2.82	0.9976	2.32	0.9898	1.82	0.9656	1.32	0.9066	0.82	0.7939	0.32	0.6255
3.31	0.9995	2.81	0.9975	2.31	0.9896	1.81	0.9649	1.31	0.9049	0.81	0.7910	0.31	0.6217
3.3	0.9995	2.8	0.9974	2.3	0.9893	1.8	0.9641	1.3	0.9032	0.8	0.7881	0.3	0.6179
3.29	0.9995	2.79	0.9974	2.29	0.9890	1.79	0.9633	1.29	0.9015	0.79	0.7852	0.29	0.6141
3.28	0.9995	2.78	0.9973	2.28	0.9887	1.78	0.9625	1.28	0.8997	0.78	0.7823	0.28	0.6103
3.27	0.9995	2.77	0.9972	2.27	0.9884	1.77	0.9616	1.27	0.8980	0.77	0.7794	0.27	0.6064
3.26	0.9994	2.76	0.9971	2.26	0.9881	1.76	0.9608	1.26	0.8962	0.76	0.7764	0.26	0.6026
3.25	0.9994	2.75	0.9970	2.25	0.9878	1.75	0.9599	1.25	0.8944	0.75	0.7734	0.25	0.5987
3.24	0.9994	2.74	0.9969	2.24	0.9875	1.74	0.9591	1.24	0.8925	0.74	0.7704	0.24	0.5948
3.23	0.9994	2.73	0.9968	2.23	0.9871	1.73	0.9582	1.23	0.8907	0.73	0.7673	0.23	0.5910
3.22	0.9994	2.72	0.9967	2.22	0.9868	1.72	0.9573	1.22	0.8888	0.72	0.7642	0.22	0.5871
3.21	0.9993	2.71	0.9966	2.21	0.9864	1.71	0.9564	1.21	0.8869	0.71	0.7611	0.21	0.5832
3.2	0.9993	2.7	0.9965	2.2	0.9861	1.7	0.9554	1.2	0.8849	0.7	0.7580	0.2	0.5793
3.19	0.9993	2.69	0.9964	2.19	0.9857	1.69	0.9545	1.19	0.8830	0.69	0.7549	0.19	0.5753
3.18	0.9993	2.68	0.9963	2.18	0.9854	1.68	0.9535	1.18	0.8810	0.68	0.7517	0.18	0.5714
3.17	0.9992	2.67	0.9962	2.17	0.9850	1.67	0.9525	1.17	0.8790	0.67	0.7486	0.17	0.5675
3.16	0.9992	2.66	0.9961	2.16	0.9846	1.66	0.9515	1.16	0.8770	0.66	0.7454	0.16	0.5636
3.15	0.9992	2.65	0.9960	2.15	0.9842	1.65	0.9505	1.15	0.8749	0.65	0.7422	0.15	0.5596
3.14	0.9992	2.64	0.9959	2.14	0.9838	1.64	0.9495	1.14	0.8729	0.64	0.7389	0.14	0.5557
3.13	0.9991	2.63	0.9957	2.13	0.9834	1.63	0.9484	1.13	0.8708	0.63	0.7357	0.13	0.5517
3.12	0.9991	2.62	0.9956	2.12	0.9830	1.62	0.9474	1.12	0.8686	0.62	0.7324	0.12	0.5478
3.11	0.9991	2.61	0.9955	2.11	0.9826	1.61	0.9463	1.11	0.8665	0.61	0.7291	0.11	0.5438
3.1	0.9990	2.6	0.9953	2.1	0.9821	1.6	0.9452	1.1	0.8643	0.6	0.7257	0.1	0.5398
3.09	0.9990	2.59	0.9952	2.09	0.9817	1.59	0.9441	1.09	0.8621	0.59	0.7224	0.09	0.5359
3.08	0.9990	2.58	0.9951	2.08	0.9812	1.58	0.9429	1.08	0.8599	0.58	0.7190	0.08	0.5319
3.07	0.9989	2.57	0.9949	2.07	0.9808	1.57	0.9418	1.07	0.8577	0.57	0.7157	0.07	0.5279
3.06	0.9989	2.56	0.9948	2.06	0.9803	1.56	0.9406	1.06	0.8554	0.56	0.7123	0.06	0.5239
3.05	0.9989	2.55	0.9946	2.05	0.9798	1.55	0.9394	1.05	0.8531	0.55	0.7088	0.05	0.5199
3.04	0.9988	2.54	0.9945	2.04	0.9793	1.54	0.9382	1.04	0.8508	0.54	0.7054	0.04	0.5160
3.03	0.9988	2.53	0.9943	2.03	0.9788	1.53	0.9370	1.03	0.8485	0.53	0.7019	0.03	0.5120
3.02	0.9987	2.52	0.9941	2.02	0.9783	1.52	0.9357	1.02	0.8461	0.52	0.6985	0.02	0.5080
3.01	0.9987	2.51	0.9940	2.01	0.9778	1.51	0.9345	1.01	0.8438	0.51	0.6950	0.01	0.5040
3	0.9987	2.5	0.9938	2	0.9772	1.5	0.9332	1	0.8413	0.5	0.6915	0	0.5000

Table A4.1 Standardised normal distribution (continued)

Z	p	Z	p	Z	p	Z	p	Z	p	Z	p	Z	p
-3.49	0.0002	-2.99	0.0014	-2.49	0.0064	-1.99	0.0233	-1.49	0.0681	-0.99	0.1611	-0.49	0.3121
-3.48	0.0003	-2.98	0.0014	-2.48	0.0066	-1.98	0.0239	-1.48	0.0694	-0.98	0.1635	-0.48	0.3156
-3.47	0.0003	-2.97	0.0015	-2.47	0.0068	-1.97	0.0244	-1.47	0.0708	-0.97	0.1660	-0.47	0.3192
-3.46	0.0003	-2.96	0.0015	-2.46	0.0069	-1.96	0.0250	-1.46	0.0721	-0.96	0.1685	-0.46	0.3228
-3.45	0.0003	-2.95	0.0016	-2.45	0.0071	-1.95	0.0256	-1.45	0.0735	-0.95	0.1711	-0.45	0.3264
-3.44	0.0003	-2.94	0.0016	-2.44	0.0073	-1.94	0.0262	-1.44	0.0749	-0.94	0.1736	-0.44	0.3300
-3.43	0.0003	-2.93	0.0017	-2.43	0.0075	-1.93	0.0268	-1.43	0.0764	-0.93	0.1762	-0.43	0.3336
-3.42	0.0003	-2.92	0.0018	-2.42	0.0078	-1.92	0.0274	-1.42	0.0778	-0.92	0.1788	-0.42	0.3372
-3.41	0.0003	-2.91	0.0018	-2.41	0.0080	-1.91	0.0281	-1.41	0.0793	-0.91	0.1814	-0.41	0.3409
-3.4	0.0003	-2.9	0.0019	-2.4	0.0082	-1.9	0.0287	-1.4	0.0808	-0.9	0.1841	-0.4	0.3446
-3.39	0.0003	-2.89	0.0019	-2.39	0.0084	-1.89	0.0294	-1.39	0.0823	-0.89	0.1867	-0.39	0.3483
-3.38	0.0004	-2.88	0.0020	-2.38	0.0087	-1.88	0.0301	-1.38	0.0838	-0.88	0.1894	-0.38	0.3520
-3.37	0.0004	-2.87	0.0021	-2.37	0.0089	-1.87	0.0307	-1.37	0.0853	-0.87	0.1922	-0.37	0.3557
-3.36	0.0004	-2.86	0.0021	-2.36	0.0091	-1.86	0.0314	-1.36	0.0869	-0.86	0.1949	-0.36	0.3594
-3.35	0.0004	-2.85	0.0022	-2.35	0.0094	-1.85	0.0322	-1.35	0.0885	-0.85	0.1977	-0.35	0.3632
-3.34	0.0004	-2.84	0.0023	-2.34	0.0096	-1.84	0.0329	-1.34	0.0901	-0.84	0.2005	-0.34	0.3669
-3.33	0.0004	-2.83	0.0023	-2.33	0.0099	-1.83	0.0336	-1.33	0.0918	-0.83	0.2033	-0.33	0.3707
-3.32	0.0005	-2.82	0.0024	-2.32	0.0102	-1.82	0.0344	-1.32	0.0934	-0.82	0.2061	-0.32	0.3745
-3.31	0.0005	-2.81	0.0025	-2.31	0.0104	-1.81	0.0351	-1.31	0.0951	-0.81	0.2090	-0.31	0.3783
-3.3	0.0005	-2.8	0.0026	-2.3	0.0107	-1.8	0.0359	-1.3	0.0968	-0.8	0.2119	-0.3	0.3821
-3.29	0.0005	-2.79	0.0026	-2.29	0.0110	-1.79	0.0367	-1.29	0.0985	-0.79	0.2148	-0.29	0.3859
-3.28	0.0005	-2.78	0.0027	-2.28	0.0113	-1.78	0.0375	-1.28	0.1003	-0.78	0.2177	-0.28	0.3897
-3.27	0.0005	-2.77	0.0028	-2.27	0.0116	-1.77	0.0384	-1.27	0.1020	-0.77	0.2206	-0.27	0.3936
-3.26	0.0006	-2.76	0.0029	-2.26	0.0119	-1.76	0.0392	-1.26	0.1038	-0.76	0.2236	-0.26	0.3974
-3.25	0.0006	-2.75	0.0030	-2.25	0.0122	-1.75	0.0401	-1.25	0.1056	-0.75	0.2266	-0.25	0.4013
-3.24	0.0006	-2.74	0.0031	-2.24	0.0125	-1.74	0.0409	-1.24	0.1075	-0.74	0.2296	-0.24	0.4052
-3.23	0.0006	-2.73	0.0032	-2.23	0.0129	-1.73	0.0418	-1.23	0.1093	-0.73	0.2327	-0.23	0.4090
-3.22	0.0006	-2.72	0.0033	-2.22	0.0132	-1.72	0.0427	-1.22	0.1112	-0.72	0.2358	-0.22	0.4129
-3.21	0.0007	-2.71	0.0034	-2.21	0.0136	-1.71	0.0436	-1.21	0.1131	-0.71	0.2389	-0.21	0.4168
-3.2	0.0007	-2.7	0.0035	-2.2	0.0139	-1.7	0.0446	-1.2	0.1151	-0.7	0.2420	-0.2	0.4207
-3.19	0.0007	-2.69	0.0036	-2.19	0.0143	-1.69	0.0455	-1.19	0.1170	-0.69	0.2451	-0.19	0.4247
-3.18	0.0007	-2.68	0.0037	-2.18	0.0146	-1.68	0.0465	-1.18	0.1190	-0.68	0.2483	-0.18	0.4286
-3.17	0.0008	-2.67	0.0038	-2.17	0.0150	-1.67	0.0475	-1.17	0.1210	-0.67	0.2514	-0.17	0.4325
-3.16	0.0008	-2.66	0.0039	-2.16	0.0154	-1.66	0.0485	-1.16	0.1230	-0.66	0.2546	-0.16	0.4364
-3.15	0.0008	-2.65	0.0040	-2.15	0.0158	-1.65	0.0495	-1.15	0.1251	-0.65	0.2578	-0.15	0.4404
-3.14	0.0008	-2.64	0.0041	-2.14	0.0162	-1.64	0.0505	-1.14	0.1271	-0.64	0.2611	-0.14	0.4443
-3.13	0.0009	-2.63	0.0043	-2.13	0.0166	-1.63	0.0516	-1.13	0.1292	-0.63	0.2643	-0.13	0.4483
-3.12	0.0009	-2.62	0.0044	-2.12	0.0170	-1.62	0.0526	-1.12	0.1314	-0.62	0.2676	-0.12	0.4522
-3.11	0.0009	-2.61	0.0045	-2.11	0.0174	-1.61	0.0537	-1.11	0.1335	-0.61	0.2709	-0.11	0.4562
-3.1	0.0010	-2.6	0.0047	-2.1	0.0179	-1.6	0.0548	-1.1	0.1357	-0.6	0.2743	-0.1	0.4602
-3.09	0.0010	-2.59	0.0048	-2.09	0.0183	-1.59	0.0559	-1.09	0.1379	-0.59	0.2776	-0.09	0.4641
-3.08	0.0010	-2.58	0.0049	-2.08	0.0188	-1.58	0.0571	-1.08	0.1401	-0.58	0.2810	-0.08	0.4681
-3.07	0.0011	-2.57	0.0051	-2.07	0.0192	-1.57	0.0582	-1.07	0.1423	-0.57	0.2843	-0.07	0.4721
-3.06	0.0011	-2.56	0.0052	-2.06	0.0197	-1.56	0.0594	-1.06	0.1446	-0.56	0.2877	-0.06	0.4761
-3.05	0.0011	-2.55	0.0054	-2.05	0.0202	-1.55	0.0606	-1.05	0.1469	-0.55	0.2912	-0.05	0.4801
-3.04	0.0012	-2.54	0.0055	-2.04	0.0207	-1.54	0.0618	-1.04	0.1492	-0.54	0.2946	-0.04	0.4840
-3.03	0.0012	-2.53	0.0057	-2.03	0.0212	-1.53	0.0630	-1.03	0.1515	-0.53	0.2981	-0.03	0.4880
-3.02	0.0013	-2.52	0.0059	-2.02	0.0217	-1.52	0.0643	-1.02	0.1539	-0.52	0.3015	-0.02	0.4920
-3.01	0.0013	-2.51	0.0060	-2.01	0.0222	-1.51	0.0655	-1.01	0.1562	-0.51	0.3050	-0.01	0.4960
-3	0.0013	-2.5	0.0062	-2	0.0228	-1.5	0.0668	-1	0.1587	-0.5	0.3085	0	0.5000

ANNEX 5

MEASUREMENT METHODS FOR CHEMICAL AGENTS IN THE LIST OF INDICATIVE LIMIT VALUES IN DIRECTIVE 2000/39/EC

1. SAMPLING AND ANALYTICAL METHODS

In order to obtain reliable results when measuring chemical agents for which there is an occupational exposure limit value (LV), it is necessary to use methods which have appropriate characteristics, to apply these in accordance with the instructions and recommendations included therein and to appropriately monitor all stages of implementation of the method.

The European standards produced by CEN Technical Committee 137[35] "*Assessment of workplace exposure*" lay down minimum requirements for the characteristics of measurement methods which establish their suitability for determining concentrations of chemical substances in workplace air.

According to EN 482:1994, measurements which are intended to be compared with occupational exposure limit values are those which *"provide accurate and reliable information on, or allow the prediction of, the time-weighted average concentration of a specific chemical agent in the air which may be inhaled"*. Therefore, as indicated in the aforementioned standard, the overall uncertainty in these measurements must be ≤ 30% for the range from 0.5 to 2 LV and ≤ 50% for the range from 0.1 to 0.5 LV. The measurement method must meet these requirements with sampling times which are the same as, or less than, the reference period for the limit value in the typical environmental conditions of workplaces. In addition to this, procedures and equipment used in the measurement of chemical substances must comply with the specific standards resulting from EN 482:1994 which apply in individual circumstances (see sections 2.1 and 2.2 of this Annex and Part III (Bibliography) of these Practical Guidelines).
Methods which normally meet the above requirements are methods having separate stages of sampling and analysis. A Sampling and Analytical Method (SAM) is a specific set of working procedures or operations allowing a requirement for specific measurement to be met, such as determining the concentration of a chemical agent in air or in a specific matrix.

Three stages can be distinguished in sampling and analytical methods:

- sampling, in which the procedure which must be used in order to obtain samples is indicated,
- transport and storage, in which precautions and recommendations to prevent alterations in the samples once they have been obtained are indicated, and
- analysis, which describes the treatment to be applied to the samples in the laboratory.

Methods are basically defined by:

- the specific substance (or substances) being measured,
- the sampling system (active/passive, collection medium, etc.),
- the analytical technique used.

The sampling and analytical methods included in this document were selected on the basis of the extent to which they comply with European standards. The starting point was existing published methods, written in a standard form, with known validation protocols and accessible validation reports. The characteristics of the methods selected were compared with the requirements of the European standards in order to determine their suitability. Validation protocols vary depending on their origin, as a result of which it was necessary to estimate some of the parameters included in the European standards on the basis of the available information.

[35] European Committee for Standardisation

2. REQUIREMENTS OF MEASUREMENT METHODS

2.1 GENERAL REQUIREMENTS

The general requirements, contained in EN 482:1994, for measurements of chemical agents in the workplace, intended for comparison with the limit values (LV), are as follows:

Minimum specified measuring range. The measuring range of the measuring procedure must take account of the limit value and be between 0.1 LV and 2 LV. This means that, throughout this range, the overall uncertainty must be within the specified limits (see below for the definition of overall uncertainty).

Averaging time. This is the period of time for which the measuring procedure yields an individual result. For a method with separate sampling and analytical stages, the averaging time is equivalent to the sampling time. For measurement methods intended for comparison with the limit values, the sampling time must be less than or equal to the reference period of the limit value.

Overall uncertainty. In general, measuring uncertainty is defined as the estimate characterising the range of values within which, generally with a given high probability, the true value of the magnitude measured lies [UNE-EN 30012-1, 3.7:1994]. In the field of chemical agent measurement, the term *overall uncertainty* is used to define the quantity used to characterise, as a whole, the uncertainty of the result given by a measuring procedure or apparatus. It is quantitatively expressed, as a percentage, by a combination of bias and precision, generally according to the formula [UNE-EN 482:1994, 3.7:1995]:

$$\frac{\left|\overline{X} - X_{ref}\right| + 2s}{X_{ref}} \times 100$$

where:

$\overline{X}$ is the mean value of the results of a number n of repeated measurements;

X_{ref} is the true or accepted reference value of the concentration;

s is the standard deviation of the measurements.

The overall uncertainty, calculated according to the above formula, must be ≤ 30% for the range of 0.5 LV to 2 LV and ≤ 50% for the range of 0.1 LV to 0.5 LV.

Physical and chemical integrity of the sample. Storage and transport must occur in such a way that the physical and chemical integrity of the sample is maintained. The method must include the transport and storage conditions (temperature, protection from light, maximum storage time, etc.).

Environmental conditions. The above requirements should be met under the environmental conditions present at the workplace and typical for the intended use of the procedure. Normally, information on the influence of the temperature in the 5-40ºC range, moisture in the 20-80% range of relative humidity, pressure and other parameters are taken into account.

Selectivity. Selectivity is defined as the degree of independence of the method from interferents [UNE-EN 482, 3.9:1995]. It is also defined as the degree by which a method can determine a particular analyte within a complex mixture, without suffering any interference from other components in the mixture [WELAC/EURACHEM:93]. The measuring procedure must take account of the possible interferents and provide information to minimise their effects.

Description of method. The description of the method will preferably follow the guidelines in ISO 78/2: 1982 (see Part III). The description must contain all the information needed to carry out the procedure with an indication, in addition, of the overall uncertainty achievable, measuring range, averaging time, interferents and information on the environmental or other conditions which may have an influence.

The formal composition of the method according to the guidelines in ISO 78/2:1982 sets out the information in the following sections:

- Introduction (optional)
- Object and scope
- Definitions
- Basis of method
- Reagents and products
- Apparatus and material
- Sampling
- Analytical procedure
- Calculations
- Precision and accuracy
- Bibliography

Expression of the results. The final result provided by the measurement method must be expressed in the same units as the limit value.

2.2 SPECIFIC REQUIREMENTS

In addition to the general requirements, and depending on the physical state of the chemical agent in the atmosphere, its chemical nature, the kind of chemical agent which must be measured, the type of sampling (active or passive) and the collection medium, reference should be made to the standards indicated below (see Part III):

- For all methods using active sampling systems, personal sampling pumps shall comply with EN 1232:1997 and pumps for flows in excess of 5 l/min with EN 12919: 1999.

- The methods for determining chemical agents present in the atmosphere as gases and vapours shall also comply with the requirements of EN 1076:1997 if sorbent tubes are used or EN 838:1995 in the case of passive (diffusive) samplers.

- Methods for determining chemical agents present in the atmosphere as particles and which require size selectors must comply with EN 481:1993 and EN 13205:2001. Methods for determining metals and metalloids must also comply with the requirements of EN 13890:2002 and methods for determining chemical agents present as mixtures of particles and vapours must comply with the requirements of ENV 13936:2001.

2.3 VALIDATION OF THE METHOD

The methods to be used must be validated methods which ensure that results are obtained with the required level of reliability. The validation of a measurement procedure establishes, as a result of systematic laboratory studies, that the characteristics of the procedure comply with the specifications

relating to the intended use of the analytical results. The validation process provides information on the functional characteristics of the method and provides a high degree of confidence in this and in the results obtained when it is applied.

In order to establish methods for determining the concentration of chemical contaminants it is necessary to establish a number of behaviour criteria in advance which include, among other values, the maximum bias and precision values which must be achieved under laboratory conditions similar to actual conditions. These criteria, which must also include possible environmental influences, normally take the form of documents known as Validation Protocols.

A validation protocol must be such as to permit the overall uncertainty (precision and bias) of the method to be determined and must be based on measurements repeated under specified conditions. The minimum number of repeated measurements for a given set of conditions is six. The relative overall uncertainty must be determined at concentrations corresponding to the upper and lower limits of the minimum specified measuring range (0.1 LV to 2 LV) and at a minimum of one other intermediate concentration.

Depending on the basis of the method, the protocol should include a test of the influence of environmental parameters and interferents which might affect the results of a measurement. In addition to this, other factors whose influence should be taken into account where necessary, such as wind speed and direction or the direction of the air inlet orifice when sampling, need to be taken into consideration. If correction factors are applied to a known bias which can be explained as a result of environmental influences, these factors must be justified and recorded in the validation report.

2.4 OTHER CHARACTERISTICS TO BE EVALUATED

Among the non-technical characteristics, it may be particularly interesting to users to have access to an evaluation of the difficulty of applying the method and the financial cost of the instrumentation needed. Evaluation of these characteristics is very much dependent on the situation of the organisation carrying out the measurements and the workplace to be evaluated, and also the number of measurements (samples to be taken and analysed) and the number of determinations (analytes) per sample.

Degree of difficulty. The following factors are taken into consideration in order to evaluate the difficulty in applying each of the selected methods:

- The necessary equipment and accessories are commercially available.
- Calibration standards can be prepared simply by dissolution.
- There are no limitations or difficulties with regard to sampling (for example, use of bubblers).
- No overly long minimum sampling periods (for example, 4 hours or more) are required.
- The transport and storage of samples do not require any special precautions apart from the general precautions indicated in the next chapter and “store at 4°C”.
- There are no restrictions or limitations on conditions throughout the scope of the method.
- The analyte is stable and there are no trends in the overall uncertainty values relating to concentration or other conditions.

The categories used in relation to the degree of difficulty are**:** simple application, complex application and very complex application. *Simple application* is if the characteristics indicated above are met and *Complex application* and *Very complex application* are if two or more than two of the above conditions are not met (this would be the case with a method requiring an impregnated collection medium which is not commercially available).

Financial cost. Although chemical analysis equipment is normally much more expensive than that used for sampling, this is considered as a whole in order to estimate the financial cost. The following criteria are used.

- *Low* (< 12 000 euros)
- *Medium* (from 12 000 to 42 000 euros)
- *High* (> 42 000 euros)

3. GENERAL RECOMMENDATIONS FOR APPLYING THE METHOD

The three parts forming the measurement method (sampling, transport and storage and instrumental analysis) are normally carried out by different persons which means that systems ensuring sample integrity and safekeeping throughout the process must be available.

3.1 SAMPLING

Sampling is required for all analytical determinations which must be carried out in a laboratory. This is the first stage in the measurement method and is completely separate from the analytical determination both due to the different specific problems and the different way in which it is carried out over time, and in most cases by different operators. However, both sampling and analytical determination are wholly related to and dependent on each other.

Sampling must be carried out according to the instructions for the measurement method selected. Before carrying this out, it is necessary to ensure that the equipment used is adequately calibrated and maintained and that the collection media are those recommended in the method, that they have been stored under the conditions recommended by the manufacturer and that they have not passed their expiry date where appropriate.

In the case of passive (diffusive) sampling, it must be borne in mind that the collection rate indicated in the method is only valid for the model of sampler used in the validation. If a different sampler model is used, the user must calculate the collection rate or obtain this from the manufacturer.

It is important for samples to be unequivocally identified and for all pertinent data and information on the workplace to be gathered. Likewise, there should be a record of samples in which at least the assigned reference number, the place where they were taken, the equipment used, the sampling conditions, the person who carried out the sampling and the laboratories to which the samples are sent for analysis must be recorded.

3.2 SAMPLE TRANSPORT AND STORAGE

The part of the measurement method which includes the transport and storage or safekeeping of samples is of vital importance, as inappropriate treatment of samples during this stage will affect their integrity and invalidate the entire measurement process. To give continuous assurance that the samples are in an appropriate condition, special care must be taken to ensure that there are no times and places when or where no one is responsible for the samples taken (they are not in safekeeping).

The measurement method lays down the conditions of transport and storage which must be complied with: temperature, protection from light, recommended humidity and maximum storage time. It is desirable that the time between sampling and receipt by the laboratory carrying out the analysis should be as short as possible.

The main recommendations are:

- Seal or enclose samples immediately after collection.
- Package samples in suitable containers for transport.
- Include a "blank sample" (a sample through which no air has been passed) with each lot of samples.
- Do not place environmental samples and raw materials samples (bulk samples) in the same box or container.
- Prevent samples from altering due to excessive heating or intense exposure to sunlight.
- Do not store samples; send them to the laboratory immediately.
- Store samples appropriately according to the instructions of the analytical method and do not handle them until the time when they are to be analysed.

3.3 ANALYSIS

It is appropriate that the laboratory carrying out the analyses should comply with the requirements of EN-ISO/CEI 17025: 1999, especially as regards the following aspects:

- Have a quality system in place.
- Have a plan for maintaining and calibrating equipment.
- Apply Standard Operating Procedures (SOPs) in the activities.
- Use validated measurement methods.
- Have personnel with the necessary training and experience.
- Participate in external quality evaluation programmes or inter-laboratory comparison tests.

4. METHOD SELECTION AND EVALUATION

4.1 COLLECTIONS OF SAMPLING AND ANALYTICAL METHODS

The sampling and analytical methods for the chemical agents covered by Directive 2000/39/EC were selected from existing published methods, written in a standard form, with known validation protocols and accessible validation reports.

For this purpose, collections of methods published by the competent institutions of EU countries cited in EN 14042:2003 were considered in the first stage of selection. From these, those methods for which the validation protocols and validation data had been published or were accessible were included, wherever possible. The collections of methods considered are those cited in Part III of this document (Bibliography).

The methods in these collections provide, in many cases, specific published validation protocols or validation results. If not, the NIOSH and OSHA validation data are used. It has therefore been necessary to use the NIOSH and OSHA collections of methods because they are the general reference in most EU countries, even where published collections of methods are available. The NIOSH and OSHA collections of methods are also found among the references of EN 14042:2003. These institutions publish both the validation protocols and the results of the validation process.

In some cases, where the information was insufficient, it has been necessary to use articles published in scientific journals.

4.2 GATHERING OF INFORMATION ON THE METHODS FOR EACH CHEMICAL AGENT

More than one published method is available for many substances. These may be the same or equivalent methods or different methods. Methods are considered to be the same or equivalent when the sampling and analytical method and equipment used are the same and the procedures are similar. There may be differences in the scope of identical or equivalent methods due to differences in limit values, as a result both of differences existing between values established in different countries and of amendments (normally reductions, sometimes drastic) in limit values over time.

For each identical method or group of identical methods, tables similar to that given below (Table A5.1) contain all the available data, both that from the method itself and that from the corresponding validation reports, in order to provide information on the scope, sampling, transport and storage and analysis and any other information of interest.

Table A5.1 Collection of information for each method

(Name of Chemical Agent)	**LV (8 h) =**	**mg/m^3, LV (short-term) =**		**mg/m^3**
		Method 1	Method 2	Method 3
Breakthrough volume	Concentration in atmosphere mg/m^3 (x LV)			
	Relative Humidity (%)			
	Flow rate (l/min)			
Desorption efficiency	Added mass (mg per sample)			
Tests Sampling/analysis	Flow rate (l/min)			
	Sample volume (l)			
	Concentration in atmosphere mg/m^3 (x LV)			
	Relative Humidity (%)			
	mg collected			
Storage test	Concentration in atmosphere mg/m3 (x LV)			
	Relative Humidity (%)			
	Storage conditions (Refrigerated / ambient)			
	Storage time (days)			
Other information	Interferents, limitations, etc.			

4.3 METHOD EVALUATION

The methods were evaluated according to the extent with which they comply with the requirements indicated in Section 2, with identical or equivalent methods being grouped together. Operating characteristics (techniques) were evaluated first followed by other characteristics. The characteristics of the possible method were compared with the requirements laid down in the European standards. The requirements of EN 482:1994 for measurements intended for comparison with limit values were used as a

basic and general reference (Section 2.1). All the specific standards deriving from EN 482:1994, cited above in 2.2, and detailing requirements for different types of procedures and equipment used for the measurement of chemical substances, were also considered.

Available validation information was also considered when evaluating and selecting methods. Validation protocols vary according to their origin, so it was necessary to estimate some of the parameters indicated in the European standards on the basis of available information. EN 482:1994 indicates that methods for comparison with LVs must be validated within a range of 0.1 to 2 LV. This criterion, which is based on the LV, means that the operating range must change whenever the limit value changes. The published methods have been validated, at least in some cases, for limit values which are substantially higher and sometimes lower than the LVs in the Directive and in all cases for an eight-hour LV. This means that the validation conditions had to be extrapolated to current needs in order to take advantage of validation work carried out on the methods in the past. Therefore, where necessary, the sample volume has been adapted to ensure that the absolute sample quantities collected at the recommended flow rate lie within the concentration range referred to in the validation data. In the case of organic solvents collected on a solid adsorbent, such extrapolation is possible provided that certain fundamental validation concepts such as breakthrough volume are respected. In practice this consists of ensuring that the adsorption capacity of the adsorbent used, which would invalidate the sample collected, is not exceeded.

5. SAMPLING AND ANALYTICAL METHOD SHEETS FOR THE CHEMICAL AGENTS IN DIRECTIVE 2000/39/EC

A sampling and analytical method sheet (in some cases two) has been produced for each chemical substance included in the list of limit values in Directive 2000/39/EC.

The sheets include fundamental information for all parts of the measurement method: sampling, transport and storage and analysis, so that they will be useful for work in the field and in the laboratory. The information is subdivided into blocks according to the model in Figure A5.2 (model sheet and explanation of contents).

In cases where there are several methods for a given substance, the data included in the sheet are those for the method selected, which is the one validated in a manner closest to the European standards for the concentration range of interest (0.1 LV to 2 LV in Directive 2000/39/EC), and the precision, bias and overall uncertainty values included are those for the method selected. Information on other methods, whether equivalent or different, is indicated in the section of the sheet on “Other methods” and, if appropriate, includes information on the relevant data from equivalent methods which may supplement the recommended method and alternative forms of sampling and analysis offered by the different methods.

Table A5.3 lists the sheets. The first column is the identification number for the sheet assigned in accordance with the order in the list of limit values in Directive 2000/39/EC. The second column is the name of the chemical agent. The third column indicates the minimum specified measuring range (defined in Section 2.1) according to EN 482:1994. The fourth column includes the validated range corresponding to the selected method indicated in the fifth column. The sixth column includes comments on limitations on the applicability of said method for measuring concentrations of hazardous chemical agents in workplace air in relation to occupational exposure limit values.

Tables A5.4 and A5.5 arrange the sheets by CAS No and in alphabetical order, respectively.

Figure A5.2 Model sheet and explanation of contents

NAME OF CHEMICAL AGENT ***Name of chemical agent from the list of LVs in Directive 2000/39/EC, sometimes followed by the synonym most currently in use.*** **CAS No:** *Chemical Abstract Service registry No*	**SHEET No --** *Order number in the list of LVs.* *Date of preparation or last update.*

LV (8 h): ----- mg/m^3, ----- ppm **LV (short-term): ----- mg/m^3, ----- ppm**
Indicative occupational exposure limit values from the Annex to Directive 2000/39/EC

SUMMARY OF METHOD

Brief description of the recommended method indicating the sampling and analytical system and basic data providing an initial general idea of the method.

SCOPE

The scale of concentrations indicating the minimum and maximum measurement levels. Expressed as a range of concentrations (mass/volume) of the chemical substance per cubic metre of air, for the recommended sample volume. The minimum and maximum concentrations correspond to 0.1 LV and 2 LV for the volume recommended.
Information available on limitations of the method, i.e. environmental conditions or other circumstances which might restrict its scope.
Information on possible applications of the method to other chemical substances.

TECHNICAL CHARACTERISTICS
Most relevant technical information for applying the method, subdivided into 4 groups: sampling, analysis, transport and storage, and data on evaluation of the method.

SAMPLING
Description of the collection system and sampling conditions.

Sampling pump: *Type of pump.*

Collection medium: *Description of characteristics.*

Recommended flow rate: ---- l/min *Flow rate of the pump used for validating the method.*

Recommended volume: --- l *Volume of air to be sampled in litres.*

ANALYSIS
Information on conditions for preparing the sample and choosing instruments.

Preparation: *Description of sample treatment.*

Technique: *Description of fundamental characteristics of the analytical technique.*

TRANSPORT AND STORAGE
Conditions (temperature, protection from light, etc.) under which samples must be transported and stored in order to maintain integrity. Indication of maximum time which can elapse before the analysis is performed under specified conditions.

METHOD EVALUATION DATA

This section includes values for operating characteristics obtained during the method validation process: precision, bias and overall uncertainty, expressed as percentages. In the case of chromatographic methods, desorption efficiency is also included as a percentage. Where the information available is incomplete or it has been necessary to make modifications to the method, or any other circumstances apply, pertinent comments are provided in the block "Other information of interest". The information differs according to the organisation issuing the method which is why it has been necessary to re-calculate some values.

Precision: --- %

Bias: --- %

Overall uncertainty: --- %

NAME OF CHEMICAL AGENT ***Name of chemical agent from the list of LVs in Directive 2000/39/EC, sometimes followed by the synonym most currently in use.*** **CAS No:** *Chemical Abstract Service registry No*	**SHEET No --** *Order number in the list of LVs.* *Date of preparation or last update.*

OTHER CHARACTERISTICS

Evaluation of the degree of difficulty and financial cost in accordance with the criteria in Section 2.3.

Degree of difficulty: *Simple application, complex application, very complex application.*
Simple application if the characteristics indicated in Section 2.3 are met and complex application and very complex application if two or more than two of the above conditions are not met. (For example, requires an impregnated collection medium which is not commercially available).

Financial cost: *low, medium, high.*
Estimated cost using only market prices for the equipment required for sampling and analysis.

OTHER INFORMATION OF INTEREST

Information on the possibility of using the method for short-term LVs.

Explanatory information on the technical characteristics of the method and its applicability. May contain some or all of the following blocks of information as appropriate:

METHOD VALIDATION INFORMATION

The concentration range for which the method has been validated, indicating the concordance with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value. Information on the conditions under which the validation tests were performed and the precision, bias and desorption efficiency (where appropriate) were obtained and study of the samples during storage.

ADAPTATION OF THE METHOD

Description of the possibility of adjusting the sample volume so that the sample quantity collected lies within the concentration range for which the method has been validated. This section is included in cases where the concentration range for which the method has been validated does not wholly or partly coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

ADDITIONAL INFORMATION AND NOTES

Additional information, warnings and notes of interest about the use of the measurement method.

REFERENCES

Bibliographic references for the method corresponding to the information included in the sheet ("recommended" method).

[1]
[2]

OTHER METHODS

References to other published methods, whether equivalent or different, including information on relevant data from equivalent methods which may supplement the recommended method and sampling and analytical alternatives offered by the methods.
The numbering of the references correlates to the previous block "References".

[3]
[4]
…….

Table A5.3 Summary of sampling and analytical methods for the substances in Directive 2000/39/EC

Sheet No	Name of chemical agent	Range 0.1 LV - 2 LV mg/m^3	Validated range mg/m^3	Method Institution – reference	Comments
1	Diethylether	30 - 616	125 – 2470	INSHT- MA 047/A01	
2	Acetone	121 -2420	130 – 2560	INSHT- MA 031/A96	
3	Chloroform	1 – 20	5 – 113	INSHT- MA 042/A99	
4	1,1,1-Trichloroethane	55 – 1110	127 – 3816	INSHT- MA 013/R87	
5	Ethylamine	0.94 – 18.8	-- - 20	OSHA - Method 36	Not applicable from 0.1 LV to 0.5 LV
6	1,1-Dichloroethane	41.2 – 824	38 – 835	INSHT- MA 043/A99	
7	Phosgene	0.008 – 0.16	-- - 1.6	OSHA - Method 61	Not applicable
8	Chlorodifluoromethane	360 – 7200	1780 – 6890	NIOSH-Method 1018-1	
9	Butanone	60 – 1200	58 – 1150	INSHT- MA 031/A96	
10	Propionic acid	3.1 – 62	- - -	OSHA -IMIS 2168	Not validated
11-1 11-2	o-Xylene	22.1 – 442	22 – 450 -- 96 --	INSHT- MA 030/A92 OSHA - Method 1002	Method validated for p-xylene (sheet No 19)
12	1,2-Dichlorobenzene	12.2 – 244	12 – 225	INSHT- MA 053/A02	
13	1,2,4-Trimethylbenzene	10 – 200	16 – 310	INSHT- MA 030/A92	
14	Cumene	10 – 200	120 – 479	NIOSH- Method 1501	Storage not studied. Effect of moisture not studied.
15	2-Phenylpropene	24.6 – 492	236 – 943	NIOSH - Method 1501	Storage not studied. Effect of moisture not studied
16-1 16-2	Ethylbenzene	44.2 – 884	49 – 942 - 73 --	INSHT- MA 030/A92 OSHA - Method 1002	
17	e-Caprolactam (dust and vapour)	1 – 20	-- - --	OSHA - Method PV 2012	Not validated
18	Heptan-3-one	9.5 – 190	100 – 463	NIOSH -Method 1301	Storage not studied. Effect of moisture not studied.
19-1 19-2	p-Xylene	22.1 – 442	50 – 850 -- 90 --	INSHT- MA 030/A92 OSHA -Method 1002	
20	1,4-Dichlorobenzene	12.2 – 244	208 – 831	NIOSH -Method 1003	Storage not studied. Effect of moisture not studied. Range not confirmed.
21	Allyl alcohol	0.48 – 9.6	1.8 – 8.4	NIOSH -Method 1402	Storage not studied. Effect of moisture not studied.
22	Ethylene glycol	5.2 - 104	- - -	OSHA -Method PV 2024	Partly validated
23	1-Methoxypropanol-2	37.5 - 750	32 – 760	INSHT- MA 017/A89	
24	4-Methylpentan-2-one	8.3 - 166	22 – 440	INSHT- MA 031/A96	
25 – 1 25 - 2	m-Xylene	22.1 – 442	50 – 850 48 - --	INSHT- MA 030/A92 OSHA - Method 1002	Method validated for p-xylene (sheet No 19)
26	2-Methoxy-1-methylethylacetate	27.5 – 450	2 – 50	INSHT- MA 024/A92	
27	Mesitylene (Trimethylbenzenes)	10 – 200	16 – 310	INSHT- MA 030/A92	Method validated for 1,2,4-trimethylbenzene (sheet No 13)
28	Chlorobenzene	4.7 – 94	4.5 – 95	INSHT- MA 042/A99	
29	Cyclohexanone	4.08 – 81.6	9.8 – 188	INSHT- MA 052/A02	

Sheet No	Name of chemical agent	Range 0.1 LV - 2 LV mg/m^3	Validated range mg/m^3	Method Institution – reference	Comments
30	Phenol	0.78 – 15.6	1.8 – 43	INSHT- MA 040/A98	
31	Tetrahydrofuran	15 –300	13 – 270	INSHT- MA 049/A01	
32	5-Methylhexan-2-one	9.5 – 190	2.29 - --	OSHA - Method PV 2042	Partly validated
33	Heptan-2-one	23.8 – 476	197- 925	NIOSH - Method 1301	Storage not studied. Effect of moisture not studied
34	Piperazine	0.01 – 0.2	---	OSHA - IMIS P 250	Not validated
35	2-Butoxyethanol	9.8 – 196	-- 96 --	OSHA - Method 83	
36	2-Butoxyethyl acetate	13.3 – 266	5 – 300	DFG - AHSA Vol. 2	Effect of moisture not studied. Lack of information on bias and storage.
37	Dimethylether	192 – 3840	190 – 3850	INSHT- MA 047/A01	
38	1,2,4-Trichlorobenzene	1.51 – 30.2	0.002 – 100	NIOSH - Method 5517	Effect of moisture not studied
39	Triethylamine	0.84 – 16.8	-- - 96	OSHA - Method PV 2060	Partly validated
40	Isopentylacetate	27- 540	24 – 550	INSHT- MA 041/A99	
41	Dimethylamine	0.38 – 7.6	7.3 – 30.6	NIOSH - Method 2010	Not applicable.
42	N,N-Dimethylacetamide	3.6 - 72	18 – 105	NIOSH - Method 2004	Effect of moisture not studied. No information on bias.
43	n-Butylacrylate	1.1 - 22	-- - 56	OSHA - Method PV 2011	Partly validated
44	n-Heptane	208.5 - 4170	134 - 2955	INSHT - MA 029/A92	
45	1,2,3-Trimethylbenzene	10 -200	15 – 310	INSHT - MA 030/A92	Method validated for 1,2,4-trimethylbenzene (sheet No 13)
46	5-Methylheptan-3-one	5.3 - 106	57 – 272	NIOSH - Method 1301	Effect of moisture not studied. Storage not studied.
47	1-Methylbutylacetate	27 - 540	24- 550	INSHT - MA 041/A99	Method validated for iso-pentylacetate (sheet No 40)
48	Pentylacetate	27 -540	24- 550	INSHT - MA 041/A99	Method validated for iso-pentylacetate
49	3-Pentylacetate	27 -540	24- 550	INSHT - MA 041/A99	Method validated for iso-pentylacetate
50	Amylacetate, tert	27 - 540	24- 550	INSHT - MA 041/A99	Method validated for iso-pentylacetate
51	Xylene, mixed isomers, pure	22.1 -442	50 – 850	INSHT- MA 030/A92	Method validated for p-xylene (sheet No 19)
52	Sulphotep	0.01 - 0.2	-- - --	NIOSH - Method 5600	Method validated for other organophosphorous pesticides
53	Hydrogen fluoride	0.15 - 3	(75 - 300)*	HSE - MDHS 35/2	Storage conditions missing.
54-1 54-2	Silver, metallic	0.01 - 0.2	(1 - 4)* (2.2-10.1)*	OSHA - Method ID-121 OSHA - Method ID-206	
55	Hydrogen chloride	0.8 -16	0.14 – 14	NIOSH - Method 7903	Sample volume not confirmed. No bias data
56	Orthophosphoric acid	0.1 - 2	(42 - 840)*	DFG - AHSA Vol. 6	
57	Ammonia, anhydrous	1.4 - 28	21.8 - 72.2	OSHA - Method ID-188	
58	Fluorine	0.158 - 3.16	-- - --	OSHA - IMIS 1270	Not validated
59	Dihydrogen selenide	0.007 - 0.14	-- - --	OSHA - IMIS 1474	Not validated
60	Hydrogen bromide	6.7 (short-term LV)	2 – 20	NIOSH - Method 7903	Not applicable to 15 min samples.
61	Sodium azide	0.01 - 0.2	0.15 - 0.71	OSHA - Method ID-211	
62	(2-Methoxymethylethoxy)-propanol	30.8 - 616	-- - 606	OSHA - Method 101	

Sheet No	Name of chemical agent	Range 0.1 LV - 2 LV mg/m^3	Validated range mg/m^3	Method Institution – reference	Comments
63	Fluorides, inorganic	0.25 - 5	G[#]: (7.5 - 300)* P[#]: (36 - 4800)*	HSE - MDHS 35/2	

* The ranges within brackets are given as micrograms per sample. In these cases the validation tests have been carried out using additional samples.

[#] G= Gaseous fluorides. P= Particulate fluorides

Table A5.4 Index by sheet No and CAS No

Sheet No	CAS No	Name of Chemical Agent
1	60-29-7	Diethylether
2	67-64-1	Acetone
3	67-66-3	Chloroform
4	71-55-6	1,1,1- Trichloroethane
5	75-04-7	Ethylamine
6	75-34-3	1,1- Dichloroethane
7	75-44-5	Phosgene
8	75-45-6	Chlorodifluoromethane
9	78-93-3	Butanone
10	79-09-4	Propionic acid
11	95-47-6	o- Xylene
12	95-50-1	1,2- Dichlorobenzene
13	95-63-6	1,2,4- Trimethylbenzene
14	98-82-8	Cumene
15	98-83-9	2- Phenylpropene
16	100-41-4	Ethylbenzene
17	105-60-2	e- Caprolactam (dust and vapour)
18	106-35-4	Heptan-3-one
19	106-42-3	p- Xylene
20	106-46-7	1,4- Dichlorobenzene
21	107-18-6	Allyl alcohol
22	107-21-1	Ethylene glycol
23	107-98-2	1- Methoxypropanol-2
24	108-10-1	4- Methylpentan-2-one
25	108-38-3	m- Xylene
26	108-65-6	2- Methoxy-1-methylethylacetate
27	108-67-8	Mesitylene (Trimethylbenzenes)
28	108-90-7	Chlorobenzene
29	108-94-1	Cyclohexanone
30	108-95-2	Phenol
31	109-99-9	Tetrahydrofuran
32	110-12-3	5- Methylhexan-2-one
33	110-43-0	Heptan-2-one
34	110-85-0	Piperazine
35	111-76-2	2- Butoxyethanol
36	112-07-2	2- Butoxyethyl acetate
37	115-10-6	Dimethylether
38	120-82-1	1,2,4- Trichlorobenzene
39	121-44-8	Triethylamine
40	123-92-2	Isopentylacetate
41	124-40-3	Dimethylamine
42	127-19-5	N,N- Dimethylacetamide
43	141-32-2	n- Butylacrylate

Sheet No	CAS No	Name of Chemical Agent
44	142-82-5	n- Heptane
45	526-73-8	1,2,3- Trimethylbenzene
46	541-85-5	5- Methylheptan-3-one
47	626-38-0	1- Methylbutylacetate
48	628-63-7	Pentylacetate
49	620-11-1	3- Pentylacetate
50	625-16-1	Amylacetate, tert
51	1330-20-7	Xylene, mixed isomers, pure
52	3689-24-5	Sulphotep
53	7664-39-3	Hydrogen fluoride
54	7440-22-4	Silver, metallic
55	7647-01-0	Hydrogen chloride
56	7664-38-2	Orthophosphoric acid
57	7664-41-7	Ammonia, anhydrous
58	7782-41-4	Fluorine
59	7783-07-5	Dihydrogen selenide
60	10035-10-6	Hydrogen bromide
61	26628-22-8	Sodium azide
62	34590-94-8	(2-Methoxymethylethoxy)-propanol
63	----	Fluorides, inorganic

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2- Butoxyethyl acetate	112-07-2	36
n- Butylacrylate	141-32-2	43
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Chloroform	67-66-3	3
Cumene	98-82-8	14
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1,1- Dichloroethane	75-34-3	6
Diethylether	60-29-7	1
Dihydrogen selenide	7783-07-5	59
N,N- Dimethylacetamide	127-19-5	42
Dimethylamine	124-40-3	41
Dimethylether	115-10-6	37
Ethylamine	75-04-7	5
Ethylbenzene	100-41-4	16
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Fluorides, inorganic	----	63
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n- Heptane	142-82-5	44
Heptan-2-one	110-43-0	33
Heptan-3-one	106-35-4	18
Hydrogen bromide	10035-10-6	60
Hydrogen chloride	7647-01-0	55
Hydrogen fluoride	7664-39-3	53
Isopentylacetate	123-92-2	40
Mesitylene (Trimethylbenzenes)	108-67-8	27
1- Methoxypropanol-2	107-98-2	23
2- Methoxy-1-methylethylacetate	108-65-6	26
(2-Methoxymethylethoxy)-propanol	34590-94-8	62
1- Methylbutylacetate	626-38-0	47
5- Methylheptan-3-one	541-85-5	46
5- Methylhexan-2-one	110-12-3	32
4- Methylpentan-2-one	108-10-1	24
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Name of chemical agent	CAS No	Sheet No
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3- Pentylacetate	620-11-1	49
Phenol	108-95-2	30
2- Phenylpropene	98-83-9	15
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Piperazine	110-85-0	34
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Silver, metallic	7440-22-4	54
Sodium azide	26628-22-8	61
Sulphotep	3689-24-5	52
Tetrahydrofuran	109-99-9	31
1,2,4- Trichlorobenzene	120-82-1	38
1,1,1- Trichloroethane	71-55-6	4
Triethylamine	121-44-8	39
1,2,3- Trimethylbenzene	526-73-8	45
1,2,4- Trimethylbenzene	95-63-6	13
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Xylene, mixed isomers, pure	1330-20-7	51

DIETHYLETHER CAS No: 60-29-7	SHEET No 1 October 2004
LV (8 h): 308 mg/m^3, 100 ppm	**LV (short-term):** 616 mg/m^3, 200 ppm

SUMMARY OF METHOD

The sample is collected by passing 8 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored at room temperature for 14 days. The diethylether is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of diethylether vapours in air, in the concentration range of 30 mg/m^3 to 620 mg/m^3, for 8 l air samples [1].

This method also allows the simultaneous determination of other ethers such as diisopropyl ether and methyl tert-butyl ether [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 8 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and SE-30 capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 100% (CV = 1.7%)

Precision: 1.2%

Bias: -5.2%

Overall uncertainty: 7.6%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

DIETHYLETHER	SHEET No 1
CAS No: 60-29-7	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of diethylether collected will be 1850 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]
The method [1] is validated for the concentration range of 125 mg/m^3 to 2470 mg/m^3. This range **does not** coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 2 l air samples, collected at 0.2 l/min in generated atmospheres, with and without moisture, in the concentration range of 125 mg/m^3 to 2470 mg/m^3 of diethylether, equivalent to 250 μg/sample and 5000 μg/sample.
The desorption efficiency corresponds to the average of 24 samples in the range of 230 μg/sample to 4200 μg/sample.

ADAPTATION OF THE METHOD:
In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.
The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **8 l** should be sampled at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.
This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] INSHT. *Determination of Ethers I (Diethylether; Diisopropyl ether; Methyl tert-butyl ether) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 047/A01.

OTHER METHODS

[2] NIOSH. *Ethyl Ether.* METHOD 1610 [*Activated charcoal tube / Gas chromatography (FID)*].

ACETONE CAS No: 67-64-1	SHEET No 2 October 2004
LV (8 h): 1210 mg/m^3, 500 ppm	**LV (short-term):**

SUMMARY OF METHOD

The sample is collected by passing 1 l of air through a tube filled with 150 / 75 mg of silica gel using a personal sampling pump at a flow rate of 0.05 l/min. The sample can be stored in a refrigerator for 14 days. The acetone is desorbed with dimethylformamide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of acetone vapours in air, in the concentration range of 130 mg/m^3 to 2570 mg/m^3, for 1 l air samples [1].

This method also allows the simultaneous determination of other ketones such as methyl ethyl ketone and methyl isobutyl ketone [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of silica gel (150 mg / 75 mg)

Sampling pump: personal type G

Recommended flow rate: 0.05 l/min

Recommended volume: 1 l

ANALYSIS

Preparation: desorption with 1 ml of dimethylformamide.

Analytical technique: gas chromatography with flame ionisation detector and SE-30 capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 101.1% (CV = 3.9%)

Precision: 2.6%

Bias: -6.7%

Overall uncertainty: 11.9%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

ACETONE	SHEET No 2
CAS No: 67-64-1	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 130 mg/m^3 to 2560 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 1 l air samples, collected at 0.05 l/min in generated atmospheres, with and without moisture, in the concentration range of 130 mg/m^3 to 2560 mg/m^3 of acetone, equivalent to 130 μg/sample and 2600 μg/sample.

The desorption efficiency corresponds to the average of 35 samples in the range of 140 μg/sample to 5000 μg/sample.

ADDITIONAL INFORMATION:

Activated charcoal should not be used for sampling acetone due to stability problems [2] [3].

The Carbosieve S-III adsorbent tube [4] may be used as an alternative collection system.

REFERENCES

[1] INSHT. *Determination of Ketones (Acetone, Methyl ethyl ketone, Methyl isobutyl ketone) in Air. Silica gel adsorption / Gas chromatography method.* MTA/MA – 031/A96.

OTHER METHODS

[2] Carl J. Elskamps *et al.* "*An alternate sampling and analytical method for 2-butanone*". Am. Ind. Hyg. Assoc. J., 44 (3), 201 (1983).

[3] J. O. Levin *et al*. "*Evaluation of solids sorbents for sampling ketones in work-room air*". Ann. Occup. Hyg., 31 (1), 31 (1987).

[4] OSHA. *Acetone.* METHOD 69 [*Carbosieve S-III tube / Gas chromatography (FID)*].

CHLOROFORM (Trichloromethane) CAS No: 67-66-3	SHEET No 3 October 2004
LV (8 h): 10 mg/m^3, 2 ppm	**LV (short-term):**

SUMMARY OF METHOD

The sample is collected by passing 60 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.2 l/min to 0.3 l/min. The sample can be stored in a refrigerator for 14 days. The chloroform is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of chloroform vapours in air, in the concentration range of 1 mg/m^3 to 20 mg/m^3, for 60 l air samples [1].

This method also allows the simultaneous determination of other chlorinated hydrocarbons such as carbon tetrachloride and chlorobenzene [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.2 l/min to 0.3 l/min

Recommended volume: 60 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 99.2% (CV = 3.9%)

Precision: 4%

Bias: 4.4%

Overall uncertainty: 12.4%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

CHLOROFORM (Trichloromethane)	SHEET No 3
CAS No: 67-66-3	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 5 mg/m^3 to 113 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 15 l air samples, collected at 0.3 l/min in generated atmospheres, with and without moisture, in the concentration range of 5 mg/m^3 to 113 mg/m^3 of chloroform, equivalent to 75 μg/sample and 1700 μg/sample.

The desorption efficiency corresponds to the average of 34 samples in the range of 77 μg/sample to 2140 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **60 l** should be sampled at a flow rate of 0.2 l/min to 0.3 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] INSHT. *Determination of Chlorinated Hydrocarbons II (Carbon tetrachloride, Chloroform, Chlorobenzene) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA / MA 042/A99.

OTHER METHODS

[2] OSHA. *Chloroform.* METHOD 5 [*Activated charcoal tube / Gas chromatography (FID)*].

[3] NIOSH. *Hydrocarbons, Halogenated.* METHOD 1003 [*Activated charcoal tube / Gas chromatography (FID)*].

1,1,1-TRICHLOROETHANE (Methyl chloroform)

CAS No: 71-55-6

SHEET No 4

October 2004

LV (8 h): 555 mg/m^3, 100 ppm

LV (short-term): 1110 mg/m^3, 200 ppm

SUMMARY OF METHOD

The sample is collected by passing 17 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored at room temperature for 14 days. The 1,1,1-trichloroethane is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 1,1,1-trichloroethane vapours in air, in the concentration range of 55 mg/m^3 to 1110 mg/m^3, for 17 l air samples [1].

This method also allows the simultaneous determination of other chlorinated hydrocarbons such as trichloroethylene and tetrachloroethylene [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 17 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and SE-30 capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 99.2% (CV = 2.2%)

Precision: 2.4%

Bias: -3.4%

Overall uncertainty: 8.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

1,1,1-TRICHLOROETHANE (Methyl chloroform) CAS No: 71-55-6	SHEET No 4 October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 1,1,1-trichloroethane collected will be 3330 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 127 mg/m^3 to 3816 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 5 l air samples, collected at 0.2 l/min in generated atmospheres, with 40% humidity, in the concentration range of 127 mg/m^3 to 3816 mg/m^3 of 1,1,1-trichloroethane, equivalent to 640 μg/sample and 19100 μg/sample.
The desorption efficiency corresponds to the average of 15 samples in the range of 940 μg/sample to 19140 μg/sample.
Inter-laboratory tests have also been conducted, in accordance with ISO 5725.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.
The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **17 l** must be sampled at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.
This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] INSHT. *Determination of Chlorinated Hydrocarbons (Trichloroethylene, Tetrachloroethylene, 1,1,1-Trichloroethane) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA 013/R87.

OTHER METHODS

[2] DFG. *1,1,1-Trichloroethane.* Analyses of Hazardous Substances in Air. Vol. 3 p. 165 [*Activated charcoal tube* / *Gas chromatography (FID)*].

[3] OSHA. *1,1,1-Trichloroethane.* METHOD 14 [*Activated charcoal tube* / *Gas chromatography (FID)*].

[4] NIOSH. *Hydrocarbons, Halogenated.* METHOD 1003 [*Activated charcoal tube* / *Gas chromatography (FID)*].

ETHYLAMINE **CAS No: 75-04-7**	**SHEET No 5** **October 2004**
LV (8 h): 9.4 mg/m^3, 5 ppm	

SUMMARY OF METHOD

The sample is collected by passing 20 l of air through a tube filled with 80 / 40 mg of XAD-7 impregnated with 10% NBD chloride (7-chloro-4-nitrobenzo-2-oxa-1,3-diazole) using a personal sampling pump at a flow rate of 0.2 l/min. The sample can be stored at room temperature for 14 days. The ethylamine is desorbed with a tetrahydrofuran solution containing 5% NBD chloride and the resulting solution is analysed in a liquid chromatograph equipped with a fluorescence and/or visible detector.

SCOPE

The method is not applicable in the range of 0.1 LV to 0.5 LV. (See "Other information of interest").

The method is applicable to the determination of ethylamine in air, in the concentration range of 5 mg/m^3 (0.5 LV) to 19 mg/m^3 (2 LV), for 20 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: tube of XAD-7 impregnated with 10% NBD chloride (7-chloro-4-nitrobenzo-2-oxa-1,3-diazole)

Sampling pump: personal type G

Recommended flow rate: 0.2 l/min

Recommended volume: 20 l

ANALYSIS

Preparation: desorb with 2 ml of tetrahydrofuran containing 5% (w/v) of NBD chloride, to which is added 25 mg of $NaHCO_3$. Stir for 30 min. and heat for 2.5 h in a 60ºC water bath. Allow to cool before analysing.

Analytical technique: liquid chromatography with fluorescence detector and Waters Radial CN column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 82.7% (CV = 2.5%)

Precision: 6.8%

Bias: -7.9%

Overall uncertainty: 21.5%

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: high

ETHYLAMINE	SHEET No 5
CAS No: 75-04-7	October 2004

OTHER INFORMATION OF INTEREST

The adsorbent tube used is not commercially available but must be prepared by the user.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration of 20 mg/m^3 (2 LV). This value coincides with the upper limit of the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value. The precision and bias shown in the sheet correspond to 10 l air samples, collected at 0.2 l/min in generated atmospheres, with 80% humidity, at a concentration of 20 mg/m^3, which is equivalent to 200 µg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 92 µg/sample to 370 µg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the range of 92 µg/sample to 370 µg/sample in which the method was studied.

To do this, at least **100 l** should be sampled for air concentrations of 0.1 LV (0.9 mg/m^3) to 0.5 LV (4.7 mg/m^3) and at least **20 l** for air concentrations of 0.5 LV (4.7 mg/m^3) to 2 LV (19 mg/m^3) at a flow rate of 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation would allow the precision and bias values obtained in the validation to be related to the concentration range of 0.5 LV to 2 LV.

NOTE

Since the collection system includes a derivatisation process, any modification to the method should be checked.

REFERENCES

[1] OSHA. *Ethylamine.* METHOD 36.

OTHER METHODS

1,1-DICHLOROETHANE

CAS No: 75-34-3

SHEET No 6

October 2004

LV (8 h): 412 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 4 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored at room temperature for 14 days. The 1,1-dichloroethane is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 1,1-dichloroethane vapours in air, in the concentration range of 38 mg/m^3 to 835 mg/m^3, for 4 l air samples [1].

This method also allows the simultaneous determination of other chlorinated hydrocarbons such as 1,2-dichloroethane and 1,2-dichloropropane [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 4 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector, and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 100.1% (CV = 0.9%)

Precision: 1.7%

Bias: -7.9%

Overall uncertainty: 11.3%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

1,1-DICHLOROETHANE	SHEET No 6
CAS No: 75-34-3	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 38 mg/m^3 to 835 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 4 l air samples, collected at 0.1 l/min in generated atmospheres, with and without moisture, in the concentration range of 38 mg/m^3 to 835 mg/m^3 of 1,1-dichloroethane, equivalent to 150 μg/sample and 3340 μg/sample.

The desorption efficiency corresponds to the average of 22 samples in the range of 120 μg/sample to 3000 μg/sample.

REFERENCES

[1] INSHT. *Determination of Chlorinated Hydrocarbons III in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA 043/A99.

OTHER METHODS

[2] NIOSH. *Hydrocarbons, Halogenated.* METHOD 1003 [*Activated charcoal tube / Gas chromatography (FID)*].

PHOSGENE (Carbonyl chloride) **CAS No: 75-44-5**	**SHEET No 7** **October 2004**
LV (8 h): 0.08 mg/m^3, 0.02 ppm	**LV (short-term):** 0.4 mg/m^3, 0.1 ppm

SUMMARY OF METHOD

The sample is collected by passing 240 l of air through a tube filled with 150 / 75 mg of XAD-2 impregnated with 2-HMP [2-(hydroxymethyl)piperidine] using a sampling pump at a flow rate of 1 l/min. The sample can be stored at room temperature for 14 days. The phosgene is desorbed with toluene and the resulting solution is analysed in a gas chromatograph equipped with a selective nitrogen / phosphorus detector.

SCOPE

The method is not applicable in the range of 0.1 LV to 2 LV. (See "Other information of interest").

The method is applicable to the determination of phosgene in air, in the concentration range of 0.2 mg/m^3 (2.5 LV) to 0.8 mg/m^3 (10 LV), for 240 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: tube of XAD-2 impregnated with 2-HMP [2-(hydroxymethyl)piperidine]

Sampling pump: multi-purpose personal

Recommended flow rate: 1 l/min

Recommended volume: 240 l

ANALYSIS

Preparation: desorption for 1 h with 1 ml of toluene.

Analytical technique: gas chromatography with nitrogen / phosphorus detector, and glass column with 10% UCON 50-HB-5100 with 2% KOH or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 19 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 94.9% (CV = 2.0%)

Precision: 3.2%

Bias: 2.8%

Overall uncertainty: 9.2%

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: medium

PHOSGENE (Carbonyl chloride)	SHEET No 7
CAS No: 75-44-5	October 2004

OTHER INFORMATION OF INTEREST

The applicability of the method for making measurements for comparison with the short-term limit value has not been confirmed.

For sampling times of 15 minutes, and at the recommended flow rate (1 l/min), the amount of phosgene collected will be 6 μg/sample, which is outside the application range for the method.

It is recommended that standards be kept at room temperature for approximately 16 h prior to analysis.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration of 1.6 mg/m^3 (20 LV). This value **does not** lie within the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value. The precision and bias shown in the sheet correspond to 60 l air samples, collected at 1 l/min in generated atmospheres, with 61% humidity, at a concentration of 1.6 mg/m^3, which is equivalent to 96 μg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 53 μg/sample to 196 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it would need to be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the range of 53 μg/sample to 196 μg/sample in which the method was studied. To do this, at least **6600 l** should be sampled for air concentrations of 0.1 LV (53 μg/sample) to 0.4 LV (211 μg/sample) and at least **1300 l** for air concentrations of 0.5 LV (52 μg/sample) to 2 LV (208 μg/sample) at a flow rate of 1 l/min, which means its use is unfeasible.

It is therefore **not** possible to relate the precision and bias values obtained in the validation to the current concentration range of interest.

NOTE

The collection system includes a derivatisation process so any modification to the method should be checked, because the collection capacity of the sampler has been shown to be affected by humidity, sampler type and flow rate.

REFERENCES

[1] OSHA. *Phosgene.* METHOD 61.

OTHER METHODS

[1] James P. Hendershott. *The simultaneous determination of chloroformates and phosgene at low concentrations in air using a solid sorbent sampling-gas chromatographic procedure***.** Am. Ind. Hyg. Assoc. J. 47(12): 742-746 (1986).

CHLORODIFLUOROMETHANE (Freon 22)

CAS No: 75-45-6

SHEET No 8

October 2004

LV (8 h): 3600 mg/m^3, 1000 ppm

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a set of two tubes filled with (400 / 200 mg) and (100 / 50 mg) of activated charcoal using a personal sampling pump at a flow rate of 0.025 l/min. The sample must be refrigerated immediately. The chlorodifluoromethane is desorbed with methylene chloride and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of chlorodifluoromethane in air, in the concentration range of 360 mg/m^3 to 7200 mg/m^3, for air samples of 1 l to 5 l [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: two tubes of activated charcoal (400 / 200 mg) and (100 / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.025 l/min

Recommended volume: 1 l to 5 l

ANALYSIS

Preparation: desorption with 20 ml of methylene chloride.

Analytical technique: gas chromatography with flame ionisation detector, and DB-1 capillary column or similar.

TRANSPORT AND STORAGE

Once sampling has been completed, samples must be refrigerated immediately and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96.5% (CV = 5.5%)

Precision: 5.5%

Bias: 1.2%

Overall uncertainty: 12.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

CHLORODIFLUOROMETHANE (Freon 22)	SHEET No 8
CAS No: 75-45-6	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 1780 mg/m^3 to 6970 mg/m^3. This range **does not** coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias of the method correspond to samples generated with a relative humidity of 80% and within a concentration range of 1780 mg/m^3 to 6970 mg/m^3.

The desorption efficiency corresponds to samples in the range of 530 μg/sample to 10400 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **5 l** should be sampled for concentrations of 0.1 LV (360 mg/m^3) to 0.5 LV (1800 mg/m^3) and at least **1 l** for concentrations of 0.5 LV (1800 mg/m^3) to 2 LV (7200 mg/m^3) at a flow rate of 0.025 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Chlorodifluoromethane.* METHOD 1018-1.

[2] SEYMOUR, M.J. *Evaluation of sampling and analytical methods for the determination of chlorodifluoromethane in air*. Am. Ind. Hyg. Assoc. J., 54: 253-259 (1993).

OTHER METHODS

2-BUTANONE (Methyl ethyl ketone) CAS No: 78-93-3	SHEET No 9 October 2004
LV (8 h): 600 mg/m^3, 200 ppm	**LV (short-term):** 900 mg/m^3, 300 ppm

SUMMARY OF METHOD

The sample is collected by passing 1 l of air through a tube filled with 150 / 75 mg of silica gel using a personal sampling pump at a flow rate of 0.05 l/min. The sample can be stored in a refrigerator for 14 days. The 2-butanone is desorbed with dimethylformamide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 2-butanone vapours in air, in the concentration range of 58 mg/m^3 to 1150 mg/m^3, for 1 l air samples.

This method also allows the simultaneous determination of other ketones such as acetone and methyl isobutyl ketone [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of silica gel (150 mg / 75 mg)

Sampling pump: personal type G

Recommended flow rate: 0.05 l/min

Recommended volume: 1 l

ANALYSIS

Preparation: desorption with 1 ml of dimethylformamide.

Analytical technique: gas chromatography with flame ionisation detector and SE-30 capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 101.8% (CV = 3.6%)

Precision: 3.3%

Bias: -5.1%

Overall uncertainty: 11.7%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

2-BUTANONE (Methyl ethyl ketone) CAS No: 78-93-3	SHEET No 9 October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the recommended flow rate (0.05 l/min), the amount of 2-butanone collected will be 675 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 58 mg/m^3 to 1150 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 1 l air samples, collected at 0.05 l/min in generated atmospheres, with and without moisture, in the concentration range of 58 mg/m^3 to 1150 mg/m^3 of 2-butanone, equivalent to 58 μg/sample and 1150 μg/sample.
The desorption efficiency corresponds to the average of 35 samples in the range of 63 μg/sample to 2000 μg/sample.

ADDITIONAL INFORMATION:

Activated charcoal must not be used for sampling 2-butanone due to stability problems [2] [3].
Carbosieve S-III [5], Anasorb 747 [6], or Anasorb CMS [7] adsorbent tubes may be used as an alternative sampling system.

REFERENCES

[1] INSHT. *Determination of Ketones (Acetone, Methyl ethyl ketone, Methyl isobutyl ketone) in Air. Silica gel adsorption / Gas chromatography method.* MTA/MA – 031/A96.

OTHER METHODS

[2] Carl J. Elskamps *et al*. "*An alternate sampling and analytical method for 2-butanone*". Am. Ind. Hyg. Assoc. J., 44(3): 201 (1983).
[3] J. O. Levin *et al*. "*Evaluation of solids sorbents for sampling ketones in work-room air*". Ann. Occup. Hyg., 31(1): 31 (1987).
[4] OSHA. *2-Butanone.* METHOD 16 [*Silica gel tube / Gas chromatography (FID)*].
[5] OSHA. *2-Butanone.* METHOD 84 [*Carbosieve S-III tube / Gas chromatography (FID)*].
[6] NIOSH. *Methyl Ethyl Ketone.* METHOD 2500 [*Anasorb 747 tube / Gas chromatography (FID)*].
[7] OSHA. *2-Butanone.* METHOD 1004 [*Anasorb CMS tube / Gas chromatography (FID)*].
[8] INRS. *Ketones I.* SHEET 020 [*Carboxen 1000 tube / Gas chromatography (FID)*].

PROPIONIC ACID **CAS No: 79-09-4**	**SHEET No 10** **October 2004**
LV (8 h): 31 mg/m^3, 10 ppm	**LV (short-term):** 62 mg/m^3, 20 ppm

SUMMARY OF METHOD

The sample is collected by passing 18 l of air through a tube filled with silica gel (520 / 260 mesh) using a personal sampling pump at a flow rate of 0.2 l/min. The propionic acid is desorbed with an acetone / water (1:1) solution and analysed in a gas chromatograph equipped with a flame ionisation detector, or by ion chromatography with a conductivity detector.

SCOPE

Not determined.

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: silica gel tube (520 / 260 mesh)

Sampling pump: personal type G

Recommended flow rate: 0.2 l/min

Recommended volume: 18 l

ANALYSIS

Preparation: desorption with an acetone / water (1:1) solution.

Analytical technique: gas chromatograph equipped with a flame ionisation detector or ion chromatography with a conductivity detector.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: no data available

Precision: no data available

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

PROPIONIC ACID CAS No: 79-09-4	SHEET No 10 October 2004

OTHER INFORMATION OF INTEREST

REFERENCES

[1] OSHA. *Chemical Sampling Information. Propionic Acid*. IMIS: 2168.

OTHER METHODS

o-XYLENE **CAS No: 95-47-6**	**SHEET No 11-1** **October 2004**
LV (8 h): 221 mg/m^3, 50 ppm	**LV (short-term):** 442 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 10 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 21 days. The o-xylene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of o-xylene vapours in air, in the concentration range of 22 mg/m^3 to 450 mg/m^3, for 10 l air samples [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as p-xylene, ethylbenzene, etc. [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA (See "Other information of interest")

Desorption efficiency: 98.5% (CV = 1%)

Precision: 1.3%

Bias: -7.6%

Overall uncertainty: 10.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

o-XYLENE	SHEET No 11-1
CAS No: 95-47-6	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of o-xylene collected will be 1326 μg/sample, which lies within the application range for the method.

METHOD VALIDATION REPORT: [1]

The desorption efficiency, precision, bias and overall uncertainty data correspond to the data obtained in the validation of p-xylene. Since o-xylene, m-xylene and p-xylene have the same limit value and are expected to behave in a similar manner during collection in activated charcoal and subsequent desorption with carbon disulphide, the same validation data are assumed for all three xylenes.

REFERENCES

[1] INSHT. *Determination of Aromatic Hydrocarbons (Benzene, Toluene, Ethylbenzene, p-Xylene, 1,2,4-Trimethylbenzene) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 030/A92.

OTHER METHODS

[2] OSHA. *Xylenes (o-, m-, p-Xylene), Ethylbenzene.* METHOD 1002 [*Activated charcoal tube / Gas chromatography (FID)*].

o-XYLENE CAS No: 95-47-6	SHEET No 11-2 October 2004
LV (8 h): 221 mg/m^3, 50 ppm	**LV (short-term):** 442 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected with a passive sampler containing 500 mg of Anasorb 747. The sample can be stored at room temperature for 16 days. The o-xylene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of o-xylene vapours in air, in the concentration range of 22 mg/m^3 to 450 mg/m^3, for samples collected by diffusion at a collection rate of 14.24 ml/min for 240 minutes.

This method also allows the simultaneous determination of other aromatic hydrocarbons such as m-xylene, p-xylene, ethylbenzene and xylene (mixed isomers) [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: passive sampler containing 500 mg of Anasorb 747

Collection rate: 14.24 ml/min

Sampling time: 240 min

ANALYSIS

Preparation: desorption with 2 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector, and DB Wax capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 89.4% (CV = 3.2%)

Precision: 0.3%

Bias: -3.5%

Overall uncertainty: 4.1%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

o-XYLENE CAS No: 95-47-6	SHEET No 11-2 October 2004

OTHER INFORMATION OF INTEREST

This method **cannot** be used to make measurements for comparison with the short-term limit value.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration of 96 mg/m^3 (0.4 LV). This value lies within the concentration range 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias data shown in the sheet correspond to 3 samples of 3.42 l, collected in a generated atmosphere with 83% relative humidity and at a concentration of 96 mg/m^3, which is equivalent to 330 μg/sample.
The desorption efficiency corresponds to the mean of 35 samples corresponding to 1.075 μg/sample, 73 μg/sample, 146 μg/sample, 292 μg/sample, 728 μg/sample, 1456 μg/sample and 2913 μg/sample.
The collection rate shown is only valid for the passive (diffusive) sampler used in the validation (SKC 575-002).

REFERENCES

[1] OSHA. *Xylenes (o-, m-, p-Xylene), Ethylbenzene.* METHOD 1002 [*Anasorb 747 passive sampler / Gas chromatography (FID)*].

OTHER METHODS

1,2-DICHLOROBENZENE **CAS No: 95-50-1**	**SHEET No 12** **October 2004**
LV (8 h): 122 mg/m^3, 20 ppm	**LV (short-term):** 306 mg/m^3, 50 ppm

SUMMARY OF METHOD

The sample is collected by passing 20 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.2 l/min. The sample can be stored at room temperature for 14 days. The 1,2-dichlorobenzene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 1,2-dichlorobenzene vapours in air, in the concentration range of 12 mg/m^3 to 230 mg/m^3, for 20 l air samples [1].

This method also allows the simultaneous determination of other chlorinated aromatic hydrocarbons such as benzyl chloride [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 20 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and SE-30 capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 89.8% (CV = 2.3%)

Precision: 2.7%

Bias: -4.7%

Overall uncertainty: 10.1%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

1,2-DICHLOROBENZENE	SHEET No 12
CAS No: 95-50-1	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 1,2-dichlorobenzene collected will be 918 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]
The method [1] is validated for the concentration range of 12 mg/m^3 to 225 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value. The precision and bias shown in the sheet correspond to 20 l air samples, collected in generated atmospheres, with and without moisture, in the concentration range of 12 mg/m^3 to 225 mg/m^3 of 1,2-dichlorobenzene, equivalent to 240 μg/sample and 4500 μg/sample.
The desorption efficiency corresponds to the average of 24 samples in the range of 250 μg/sample to 4800 μg/sample.

REFERENCES

[1] INSHT. *Determination of Aromatic Chlorinated Hydrocarbons (1,2-Dichlorobenzene, Benzyl chloride) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 053/A02.

OTHER METHODS

[2] NIOSH. *Hydrocarbons, Halogenated.* METHOD 1003 [*Activated charcoal tube / Gas chromatography (FID)*].

1,2,4-TRIMETHYLBENZENE **CAS No: 95-63-6**	**SHEET No 13** **October 2004**
LV (8 h): 100 mg/m^3, 20 ppm	

SUMMARY OF METHOD

The sample is collected by passing 8 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 21 days. The 1,2,4-trimethylbenzene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 1,2,4-trimethylbenzene vapours in air, in the concentration range of 10 mg/m^3 to 200 mg/m^3, for 8 l air samples.

This method also allows the simultaneous determination of other aromatic hydrocarbons such as benzene, toluene, ethylbenzene and p-xylene [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 8 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

A maximum of 21 days at 4ºC.

METHOD EVALUATION DATA

Desorption efficiency: 96.8% (CV = 1%)

Precision: 3.1%

Bias: -7.5%

Overall uncertainty: 13.7%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

1,2,4-TRIMETHYLBENZENE	SHEET No 13
CAS No: 95-63-6	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 16 mg/m^3 to 310 mg/m^3. This range **does not** coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 5 l air samples, collected in generated atmospheres, with and without moisture, in the concentration range of 16 mg/m^3 to 310 mg/m^3 of 1,2,4-trimethylbenzene, equivalent to 80 μg/sample and 1550 μg/sample.

The desorption efficiency corresponds to the average of 15 samples in the range of 90 μg/sample to 1500 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **8 l** should be sampled at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] INSHT. *Determination of Aromatic Hydrocarbons (Benzene, Toluene, Ethylbenzene, p-Xylene, 1,2,4-Trimethylbenzene) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 030/A92.

OTHER METHODS

CUMENE (Isopropylbenzene) **CAS No: 98-82-8**	**SHEET No 14** **October 2004**
LV (8 h): 100 mg/m^3, 20 ppm	**LV (short-term):** 250 mg/m^3, 50 ppm

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The cumene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of cumene vapours in air, in the concentration range of 10 mg/m^3 to 200 mg/m^3, for samples of 14 l to 80 l of air [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylene, naphthalene, α-methylstyrene, styrene, etc. [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 14 l to 80 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 103.2% (CV = 2.2%)

Precision: 4.2%

Bias: 3.5%

Overall uncertainty: 11.9%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

CUMENE (Isopropylbenzene) CAS No: 98-82-8	SHEET No 14 October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of cumene collected will be 750 μg/sample, which is just outside the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 120 mg/m^3 to 479 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture at a concentration of 120 mg/m^3 to 479 mg/m^3 of cumene, for 7 l air samples, equivalent to 840 μg/sample and 3353 μg/sample.
The desorption efficiency corresponds to the average of 18 samples in the range of 860 μg/sample to 3460 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **80 l** should be sampled for concentrations of 0.1 LV (10 mg/m^3) to 0.5 LV (20 mg/m^3) and at least **14 l** for concentrations of 0.5 LV (50 mg/m^3) to 2 LV (200 mg/m^3) at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Hydrocarbons, Aromatics.* METHOD 1501.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 23*. DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

2-PHENYLPROPENE (α-Methylstyrene)

CAS No: 98-83-9

SHEET No 15

October 2004

LV (8 h): 246 mg/m^3, 50 ppm

LV (short-term): 492 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The 2-phenylpropene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 2-phenylpropene vapours in air, in the concentration range of 25 mg/m^3 to 500 mg/m^3, for samples of 6 l to 25 l of air [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylene, naphthalene, cumene, styrene, etc. [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 6 l to 25 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 91.7% (CV = 1.5%)

Precision: 4.8%

Bias: -10.8%

Overall uncertainty: 20.4%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

2-PHENYLPROPENE (α-Methylstyrene) CAS No: 98-83-9	SHEET No 15 October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.

For sampling times of 15 minutes, and at the recommended flow rate (0.2 l/min), the amount of 2-phenylpropene collected will be 1476 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 236 mg/m^3 to 943 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture at a concentration of 236 mg/m^3 to 943 mg/m^3 of 2-phenylpropene, for 3 l air samples, equivalent to 700 μg/sample and 2830 μg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 687 μg/sample to 3570 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **25 l** should be sampled for concentrations of 0.1 LV (25 mg/m^3) to 0.5 LV (123 mg/m^3) and at least **6 l** for concentrations of 0.5 LV (123 mg/m^3) to 2 LV (492 mg/m^3) at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Hydrocarbons, Aromatics.* METHOD 1501.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 26.* DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

ETHYLBENZENE **CAS No: 100-41-4**	**SHEET No 16-1** **October 2004**
LV (8 h): 442 mg/m^3, 100 ppm	**LV (short-term):** 884 mg/m^3, 200 ppm

SUMMARY OF METHOD

The sample is collected by passing 5 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 21 days. The ethylbenzene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of ethylbenzene vapours in air, in the concentration range of 50 mg/m^3 to 950 mg/m^3, for 5 l air samples.

This method also allows the simultaneous determination of other aromatic hydrocarbons such as p-xylene, benzene, toluene and 1,2,4-trimethylbenzene [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 5 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 100% (CV = 1.1%)

Precision: 1.9%

Bias: -4.9%

Overall uncertainty: 8.7%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

ETHYLBENZENE	SHEET No 16-1
CAS No: 100-41-4	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of ethylbenzene collected will be 2650 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 49 mg/m^3 to 942 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 5 l air samples, collected in generated atmospheres, with and without moisture, in the concentration range of 49 mg/m^3 to 942 mg/m^3 of ethylbenzene, equivalent to 245 μg/sample and 4700 μg/sample.
The desorption efficiency corresponds to the average of 15 samples in the range of 257 μg/sample to 4000 μg/sample.

REFERENCES

[1] INSHT. *Determination of Aromatic Hydrocarbons (Benzene, Toluene, Ethylbenzene, p-Xylene, 1,2,4-Trimethylbenzene) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 030/A92.

OTHER METHODS

[2] NIOSH. *Hydrocarbons, Aromatics.* METHOD 1501 [*Activated charcoal tube / Gas chromatography (FID)*].

[3] OSHA. *Xylenes (o-, m-, p-Xylene), Ethylbenzene.* METHOD 1002 [*Activated charcoal tube / Gas chromatography (FID)*].

ETHYLBENZENE CAS No: 100-41-4	SHEET No 16-2 October 2004
LV (8 h): 442 mg/m^3, 100 ppm	**LV (short-term):** 884 mg/m^3, 200 ppm

SUMMARY OF METHOD

The sample is collected with a passive (diffusive) sampler containing 500 mg of Anasorb 747. The sample can be stored at room temperature for 16 days. The ethylbenzene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of ethylbenzene vapours in air, in the concentration range of 45 mg/m^3 to 890 mg/m^3, for samples collected by diffusion in a passive sampler at a sampling rate of 13.83 ml/min for 240 minutes [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as m-xylene, p-xylene, o-xylene and xylene (mixed isomers) [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: passive sampler containing 500 mg of Anasorb 747

Collection rate: 13.83 ml/min

Sampling time: 240 min

ANALYSIS

Preparation: desorption with 2 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and DB Wax capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 99.1% (CV = 2.8%)

Precision: 0.4%

Bias: -2.2%

Overall uncertainty: 3%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

ETHYLBENZENE	SHEET No 16-2
CAS No: 100-41-4	October 2004

OTHER INFORMATION OF INTEREST

This method **cannot** be used to make measurements for comparison with the short-term limit value.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration of 73 mg/m^3 (0.16 LV). This value lies within the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value. The precision and bias data shown in the sheet correspond to 3 samples of 3.32 l, collected in a generated atmosphere with 83% relative humidity at a concentration of 73 mg/m^3, which is equivalent to 240 μg/sample.

The desorption efficiency corresponds to the mean of 35 samples corresponding to 1.06 μg/sample, 74 μg/sample, 147 μg/sample, 294 μg/sample, 736 μg/sample, 1471 μg/sample and 2942 μg/sample.

The collection rate shown is only valid for the passive (diffusive) sampler used in the validation (SKC 575-002).

REFERENCES

[1] OSHA. *Xylenes (o-, m-, p-Xylene), Ethylbenzene.* METHOD 1002 [*Anasorb 747 passive sampler / Gas chromatography (FID)*].

OTHER METHODS

CAPROLACTAM (dust and vapour) **CAS No: 105-60-2**	**SHEET No 17** **October 2004**
LV (8 h): 10 mg/m^3	**LV (short-term):** 40 mg/m^3

SUMMARY OF METHOD

The sample is collected by passing 100 l of air through an OVS-7 sampler containing a glass-fibre filter and two sections of 270 / 140 mg of XAD-7, using a personal sampling pump at a flow rate of 1 l/min. The caprolactam is desorbed separately from the filter and from both sections of adsorbent with methanol and the resulting solutions are analysed in a liquid chromatograph equipped with an ultraviolet detector.

SCOPE

The applicability of the method has not been confirmed [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: OVS-7 sampler containing a glass-fibre filter and two sections of 270 / 140 mg of XAD-7

Sampling pump: multi-purpose personal

Recommended flow rate: 1 l/min

Recommended volume: 100 l

ANALYSIS

Preparation: each tube component is desorbed separately with 4 ml of methanol for 1 h.

Analytical technique: liquid chromatography with ultraviolet detector and 0.25 m LC-DB18 column or similar.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: no data available

Precision: no data available

Bias: no data available

Overall uncertainty:

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: high

CAPROLACTAM (dust and vapour)	SHEET No 17
CAS No: 105-60-2	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method is classed as partially validated by OSHA.

The data provided in the above method are inadequate and insufficiently conclusive for the method to be evaluated.

REFERENCES

[1] OSHA. *Caprolactam.* METHOD PV-2012.

[2] OSHA. *Chemical Sampling Information. Caprolactam (vapor)*. IMIS: 0524.

[3] OSHA. *Chemical Sampling Information. Caprolactam (dust)*. IMIS: 0523.

OTHER METHODS

3-HEPTANONE (Ethyl butyl ketone)

CAS No: 106-35-4

SHEET No 18

October 2004

LV (8 h): 95 mg/m^3, 20 ppm

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The 3-heptanone is desorbed with carbon disulphide containing 1% methanol and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 3-heptanone in air, in the concentration range of 9.5 mg/m^3 to 190 mg/m^3, for air samples of 26 l to 100 l [1].

This method also allows the simultaneous determination of other ketones such as methyl amyl ketone, mesityl oxide, etc. [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 26 l to 100 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide containing 1% methanol.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar**.**

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 94% (CV = 2.2%)

Precision: 12.5%

Bias: -3.1%

Overall uncertainty: 28.1%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

3-HEPTANONE (Ethyl butyl ketone)	SHEET No 18
CAS No: 106-35-4	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 100 mg/m^3 to 463 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture at a concentration of 100 mg/m^3 to 463 mg/m^3 of 3-heptanone, for 10 l air samples, equivalent to 1000 μg/sample and 4630 μg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 1150 μg/sample to 4600 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **100 l** should be sampled for concentrations of 0.1 LV (9.5 mg/m^3) to 0.5 LV (47 mg/m^3) and at least **26 l** for concentrations of 0.5 LV (47 mg/m^3) to 2 LV (190 mg/m^3) at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Ketones II.* METHOD 1301.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 16.* DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

p-XYLENE CAS No: 106-42-3	SHEET No 19-1 October 2004
LV (8 h): 221 mg/m^3, 50 ppm	**LV (short-term):** 442 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 10 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 21 days. The p-xylene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of p-xylene vapours in air, in the concentration range of 22 mg/m^3 to 450 mg/m^3, for 10 l air samples [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as ethylbenzene, benzene, toluene and 1,2,4-trimethylbenzene [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 98.5% (CV = 1%)

Precision: 1.3%

Bias: -7.6%

Overall uncertainty: 10.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

p-XYLENE CAS No: 106-42-3	SHEET No 19-1 October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of p-xylene collected will be 1326 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 50 mg/m^3 to 850 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 5 l air samples, collected in generated atmospheres, with and without moisture, in the concentration range of 50 mg/m^3 to 850 mg/m^3 of p-xylene, equivalent to 250 μg/sample and 4250 μg/sample.
The desorption efficiency corresponds to the average of 20 samples in the range of 257 μg/sample to 4040 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **10 l** should be sampled at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] INSHT. *Determination of Aromatic Hydrocarbons (Benzene, Toluene, Ethylbenzene, p-Xylene, 1,2,4-Trimethylbenzene) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 030/A92.

OTHER METHODS

[2] NIOSH. *Hydrocarbons, Aromatics.* METHOD 1501 [*Activated charcoal tube / Gas chromatography (FID)*].

[3] OSHA. *Xylenes (o-, m-, p-Xylene), Ethylbenzene.* METHOD 1002 [*Activated charcoal tube / Gas chromatography (FID)*].

p-XYLENE CAS No: 106-42-3	SHEET No 19-2 October 2004
LV (8 h): 221 mg/m^3, 50 ppm	**LV (short-term):** 442 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected with a passive (diffusive) sampler containing 500 mg of Anasorb 747. The sample can be stored at room temperature for 16 days. The p-xylene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of p-xylene vapours in air, in the concentration range of 45 mg/m^3 to 890 mg/m^3, for samples collected by diffusion in a passive sampler at a sampling rate of 13.94 ml/min for 240 minutes [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as m-xylene, o-xylene, ethylbenzene and xylene (mixed isomers) [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: passive (diffusive) sampler containing 500 mg of Anasorb 747

Collection rate: 13.94 ml/min

Sampling time: 240 min

ANALYSIS

Preparation: desorption with 2 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and DB Wax capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 95.3% (CV = 2.1%)

Precision: 0.5%

Bias: -3%

Overall uncertainty: 4%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

p-XYLENE CAS No: 106-42-3	SHEET No 19-2 October 2004

OTHER INFORMATION OF INTEREST

This method **cannot** be used to make measurements for comparison with the short-term limit value.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration of 90 mg/m^3 (0.4 LV). This value lies within the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value. The precision and bias data shown in the sheet correspond to 3 samples of 3.35 l, collected in a generated atmosphere with 83% relative humidity at a concentration of 90 mg/m^3, which is equivalent to 300 μg/sample.

The desorption efficiency corresponds to the mean of 35 samples corresponding to 1.54 μg/sample, 73 μg/sample, 145 μg/sample, 290 μg/sample, 725 μg/sample, 1456 μg/sample and 2902 μg/sample. The collection rate shown is only valid for the passive (diffusive) sampler used in the validation (SKC 575-002).

REFERENCES

[1] OSHA. *Xylenes (o-, m-, p-Xylene), Ethylbenzene.* METHOD 1002 [*Anasorb 747 passive sampler / Gas chromatography (FID)*].

OTHER METHODS

1,4-DICHLOROBENZENE **CAS No: 106-46-7**	**SHEET No 20** **October 2004**
LV (8 h): 122 mg/m^3, 20 ppm	**LV (short-term):** 306 mg/m^3, 50 ppm

SUMMARY OF METHOD

The sample is collected by passing a quantity of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The 1,4-dichlorobenzene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 1,4-dichlorobenzene vapours in air, in the concentration range of 10 mg/m^3 to 250 mg/m^3, for air samples of 10 l to 60 l [1].

This method also allows the simultaneous determination of other chlorinated hydrocarbons such as chloroform, chlorobenzene, 1,2-dichlorobenzene, etc. [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l to 60 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and 3 m SP 1000 column or similar.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 91.1% (CV = 2.2%)

Precision: 1.3%

Bias: -11.8%

Overall uncertainty: 14.4%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

1,4-DICHLOROBENZENE	SHEET No 20
CAS No: 106-46-7	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.

For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 1,4-dichlorobenzene collected will be 4200 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The "Documentation of the NIOSH Validation Tests" includes recovery data for three concentration levels, termed 2 LV (831 mg/m^3), 1 LV and 0.5 LV, but the exact concentration is not stated, which means that no conclusion can be drawn regarding either the precision or bias at these levels.

The method [1] is validated for the concentration range of ≈ 208 mg/m^3 to 831 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture, at a concentration of ≈ 208 mg/m^3 to 831 mg/m^3 of 1,4-dichlorobenzene, for 3 l air samples, equivalent to ≈ 625 μg/sample and 2500 μg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 676 μg/sample to 2700 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **60 l** should be sampled for concentrations of 0.1 LV (12 mg/m^3) to 0.5 LV (61 mg/m^3) and at least **10 l** for concentrations of 0.5 LV (61 mg/m^3) to 2 LV (244 mg/m^3) at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Hydrocarbons, Halogenated.* METHOD 1003.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 281*. DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

ALLYL ALCOHOL (2-propen-1-ol)

CAS No: 107-18-6

SHEET No 21

October 2004

LV (8 h): 4.8 mg/m^3, 2 ppm

LV (short-term): 12.1 mg/m^3, 5 ppm

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The allyl alcohol is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of allyl alcohol vapours in air, in the concentration range of 0.48 mg/m^3 to 9.6 mg/m^3, for air samples of 10 l to 50 l [1].

This method also allows the simultaneous determination of other alcohols such as isoamyl alcohol, cyclohexanol, diacetone alcohol, etc. [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l to 50 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and 3 m SP 1000 column or similar.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 90.1% (CV = 3.2%)

Precision: 12.4%

Bias: -4.4%

Overall uncertainty: 29.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

ALLYL ALCOHOL (2-propen-1-ol) CAS No: 107-18-6	SHEET No 21 October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.

For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of allyl alcohol collected will be 36 μg/sample, which lies within the application range.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 1.8 mg/m^3 to 8.4 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture, at a concentration of 1.8 mg/m^3 to 8.4 mg/m^3 of allyl alcohol, for 10 l air samples, equivalent to 20 μg/sample and 84 μg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 24 μg/sample to 96 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **50 l** should be sampled for concentrations of 0.1 LV (0.5 mg/m^3) to 0.5 LV (2.5 mg/m^3) and at least **10 l** for concentrations of 0.5 LV (2.5 mg/m^3) to 2 LV (9.6 mg/m^3) at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Alcohols III.* METHOD 1402.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 52.* DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

ETHYLENE GLYCOL

CAS No: 107-21-1

SHEET No 22

October 2004

LV (8 h): 52 mg/m^3, 10 ppm

LV (short-term): 104 mg/m^3, 40 ppm

SUMMARY OF METHOD

The sample is collected by passing 60 l of air through an OVS-7 sampler containing a glass-fibre filter and a tube with two sections of 270 / 140 mg of XAD-7, using a personal sampling pump at a flow rate of 1 l/min. The ethylene glycol is desorbed separately from the filter and from both sections of adsorbent with methanol and the resulting solutions are analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The applicability of the method has not been confirmed [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: OVS-7 sampler containing a glass-fibre filter and two sections of 270 / 140 mg of XAD-7

Sampling pump: multi-purpose personal

Recommended flow rate: 1 l/min

Recommended volume: 60 l

ANALYSIS

Preparation: each tube component is desorbed separately with 2 ml of methanol for 1 h.

Analytical technique: gas chromatography with flame ionisation detector and Rtx-35 capillary column or similar.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 99.5% (CV = 2.5%)

Precision: no data available

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: medium

ETHYLENE GLYCOL	SHEET No 22
CAS No: 107-21-1	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method is classed as partially validated by OSHA.

The desorption efficiency value shown in the sheet corresponds to the mean of 24 samples in the range of 146 μg/sample to 2916 μg/sample [1].

The data provided in the above method are inadequate and insufficiently conclusive for the method to be evaluated.

REFERENCES

[1] OSHA. *Ethylene glycol.* METHOD PV-2024.

OTHER METHODS

[2] NIOSH. *Glycols*. METHOD 5523 [*OVS-7 sampler / Gas chromatography (FID)*].

[3] Andersson K, Levin J.O. "*Sampling of ethylene glycol derivates in work-room air using Amberlite XAD resins*". Chemosphere 1982; 11: 1115-1119.

1-METHOXY-2-PROPANOL (Propylene glycol methyl ether) CAS No: 107-98-2	SHEET No 23 October 2004
LV (8 h): 375 mg/m^3, 100 ppm	**LV (short-term):** 568 mg/m^3, 150 ppm

SUMMARY OF METHOD

The sample is collected by passing 10 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 21 days. The 1-methoxy-2-propanol is desorbed with dichloromethane containing 5% methanol and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 1-methoxy-2-propanol vapours in air, in the concentration range of 32 mg/m^3 to 760 mg/m^3, for 10 l air samples [1].

This method also allows the simultaneous determination of other glycol ethers such as 2-ethoxyethanol [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l

ANALYSIS

Preparation: desorption with 1 ml of dichloromethane containing 5% (v/v) methanol.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 100.8% (CV = 2.9%)

Precision: 0.9%

Bias: -8.3%

Overall uncertainty: 10.1%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

1-METHOXY-2-PROPANOL (Propylene glycol methyl ether)	SHEET No 23
CAS No: 107-98-2	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.

For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 1-methoxy-2-propanol collected will be 1700 μg/sample, which lies within the application range.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 32 mg/m^3 to 760 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 10 l air samples, collected in generated atmospheres, with and without moisture, in the concentration range of 32 mg/m^3 to 760 mg/m^3 of 1-methoxy-2-propanol, equivalent to 320 μg/sample and 7600 μg/sample.

The desorption efficiency corresponds to the average of 12 samples in the range of 400 μg/sample to 7000 μg/sample.

REFERENCES

[1] INSHT. *Determination of Glycol Ethers (1-Methoxy-2-propanol, 2-Ethoxyethanol) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 017/A89.

OTHER METHODS

[2] OSHA. *Propylene Glycol Monomethyl Ethers / Acetates.* METHOD 99 [*Activated charcoal tube / Gas chromatography (FID)*].

4-METHYL-2-PENTANONE (Methyl isobutyl ketone) **CAS No: 108-10-1**	**SHEET No 24** **October 2004**
LV (8 h): 83 mg/m^3, 20 ppm	**LV (short-term):** 208 mg/m^3, 50 ppm

SUMMARY OF METHOD

The sample is collected by passing 2.5 l of air through a tube filled with 150 / 75 mg of silica gel using a personal sampling pump at a flow rate of 0.05 l/min. The sample can be stored in a refrigerator for 14 days. The 4-methyl-2-pentanone is desorbed with 1 ml of dimethylformamide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 4-methyl-2-pentanone vapours in air, in the concentration range of 8.3 mg/m^3 to 166 mg/m^3, for 2.5 l air samples [1].

This method also allows the simultaneous determination of other ketones such as acetone and methyl ethyl ketone [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of silica gel (150 mg / 75 mg)

Sampling pump: personal type G

Recommended flow rate: 0.05 l/min

Recommended volume: 2.5 l

ANALYSIS

Preparation: desorption with 1 ml of dimethylformamide.

Analytical technique: gas chromatography with flame ionisation detector and SE-30 capillary column or similar.

TRANSPORT AND STORAGE

Samples remain stable when stored in a refrigerator after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 102.7% (CV = 3.2%)

Precision: 3.4%

Bias: -5.4%

Overall uncertainty: 12.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

4-METHYL-2-PENTANONE (Methyl isobutyl ketone)	SHEET No 24
CAS No: 108-10-1	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the recommended flow rate (0.05 l/min), the amount of 4-methyl-2-pentanone collected will be 156 μg/sample, which lies within the application range.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 22 mg/m^3 to 440 mg/m^3. This range partially coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 1 l air samples, collected at 0.05 l/min in generated atmospheres, with and without moisture, in the concentration range of 22 mg/m^3 to 440 mg/m^3 of 4-methyl-2-pentanone, equivalent to 22 μg/sample and 440 μg/sample.
The desorption efficiency corresponds to the average of 35 samples in the range of 24 μg/sample to 637 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **2.5 l** should be sampled at a flow rate of 0.05 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

ADDITIONAL INFORMATION

No stability problems arise with 4-methyl-2-pentanone collected in activated charcoal and desorbed with carbon disulphide, so this can be used as an alternative for the determination of 4-methyl-2-pentanone in air [2].

REFERENCES

[1] INSHT. *Determination of Ketones (Acetone, Methyl ethyl ketone, Methyl isobutyl ketone) in Air. Silica gel adsorption / Gas chromatography method.* MTA/MA – 031/A96.

OTHER METHODS

[2] NIOSH. *Ketones I.* METHOD 1300 [*Activated charcoal tube / Gas chromatography (FID)*].

[3] INRS. *Ketones I.* SHEET 020 [*Carboxen 1000 tube / Gas chromatography (FID)*].

m-XYLENE **CAS No: 108-38-3**	**SHEET No 25-1** **October 2004**
LV (8 h): 221 mg/m^3, 50 ppm	**LV (short-term):** 442 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 10 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 21 days. The m-xylene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of m-xylene vapours in air, in the concentration range of 22 mg/m^3 to 450 mg/m^3, for 10 l air samples [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as p-xylene, ethylbenzene, etc. [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA (See "Other information of interest")

Desorption efficiency: 98.5% (CV = 1%)

Precision: 1.3%

Bias: -7.6%

Overall uncertainty: 10.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

m-XYLENE	SHEET No 25-1
CAS No: 108-38-3	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of m-xylene collected will be 1326 μg/sample, which lies within the application range for the method.

METHOD VALIDATION REPORT: [1]

The desorption efficiency, precision, bias and overall uncertainty data correspond to the data obtained in the validation of p-xylene. Since o-xylene, m-xylene and p-xylene have the same limit value and are expected to behave in a similar manner during collection in activated charcoal and subsequent desorption with carbon disulphide, the same validation data are assumed for all three xylenes.

REFERENCES

[1] INSHT. *Determination of Aromatic Hydrocarbons (Benzene, Toluene, Ethylbenzene, p-Xylene, 1,2,4-Trimethylbenzene) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 030/A92.

OTHER METHODS

[2] OSHA. *Xylenes (o-, m-, p-Xylene), Ethylbenzene.* METHOD 1002 [*Activated charcoal tube / Gas chromatography (FID)*].

m-XYLENE **CAS No: 108-38-3**	**SHEET No 25-2** **October 2004**
LV (8 h): 221 mg/m^3, 50 ppm	**LV (short-term):** 442 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected with a passive (diffusive) sampler containing 500 mg of Anasorb 747. The sample can be stored at room temperature for 16 days. The m-xylene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of m-xylene vapours in air, in the concentration range of 22 mg/m^3 to 450 mg/m^3, for samples collected by diffusion in a passive sampler at a sampling rate of 13.82 ml/min for 240 minutes [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as o-xylene, p-xylene, ethylbenzene and xylene (mixed isomers) [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: passive (diffusive) sampler containing 500 mg of Anasorb 747

Collection rate: 13.82 ml/min

Sampling time: 240 min

ANALYSIS

Preparation: desorption with 2 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and DB Wax capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 16 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96.1% (CV = 2.8%)

Precision: 0.4%

Bias: 2.8%

Overall uncertainty: 3.6%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

m-XYLENE	SHEET No 25-2
CAS No: 108-38-3	October 2004

OTHER INFORMATION OF INTEREST

This method **cannot** be used to make measurements for comparison with the short-term limit value.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration of 48 mg/m^3 (0.2 LV). This value lies within the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value. The precision and bias data shown in the sheet correspond to 3 samples of 3.32 l, collected in a generated atmosphere with 83% relative humidity at a concentration of 48 mg/m^3, which is equivalent to 160 μg/sample.

The desorption efficiency corresponds to the mean of 35 samples corresponding to 1.42 μg/sample, 73 μg/sample, 145 μg/sample, 290 μg/sample, 725 μg/sample, 1451 μg/sample and 2903 μg/sample.

The collection rate shown is only valid for the passive (diffusive) sampler used in the validation (SKC 575-002).

REFERENCES

[1] OSHA. *Xylenes (o-, m-, p-Xylene), Ethylbenzene.* METHOD 1002 [*Anasorb 747 passive sampler / Gas chromatography (FID)*].

OTHER METHODS

2-METHOXY-1-METHYLETHYLACETATE

CAS No: 108-65-6

SHEET No 26

October 2004

LV (8 h): 275 mg/m^3, 50 ppm

LV (short-term): 550 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 1 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.05 l/min. The sample can be stored in a refrigerator for 21 days. The 2-methoxy-1-methylethylacetate is desorbed with carbon disulphide containing 5% 2-butanol and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 2-methoxy-1-methylethylacetate vapours in air, in the concentration range of 27 mg/m^3 to 550 mg/m^3, for 1 l air samples [1].

This method also allows the simultaneous determination of other glycol esters such as 2-ethoxyethanol acetate [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.05 l/min

Recommended volume: 1 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide containing 5% (v/v) 2-butanol.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 100.1% (CV = 2.5%)

Precision: 2.8%

Bias: -5.5%

Overall uncertainty: 11.1%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

2-METHOXY-1-METHYLETHYLACETATE	SHEET No 26
CAS No: 108-65-6	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.

For sampling times of 15 minutes, and at the recommended flow rate (0.05 l/min), the amount of 2-methoxy-1-methylethylacetate collected will be 412 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 2 mg/m^3 to 50 mg/m^3. This range **does not** coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 10 l air samples, collected at 0.2 l/min in generated atmospheres, with and without moisture, in the concentration range of 2 mg/m^3 to 50 mg/m^3 of 2-methoxy-1-methylethylacetate, equivalent to 20 μg/sample and 500 μg/sample.

The desorption efficiency corresponds to the average of 24 samples in the range of 22 μg/sample to 482 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume and flow rate so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **1 l** should be sampled at a flow rate of 0.05 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] INSHT. *Determination of Esters II (1-Methoxy-2-propyl acetate, 2-Ethoxyethyl acetate) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 024/A92.

OTHER METHODS

[2] OSHA. *Propylene Glycol Monomethyl Ethers / Acetates.* METHOD 99 [*Activated charcoal tube / Gas chromatography (FID)*].

MESITYLENE (Trimethylbenzene)

CAS No: 108-67-8

SHEET No 27

October 2004

LV (8 h): 100 mg/m^3, 20 ppm

SUMMARY OF METHOD

The sample is collected by passing 5 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 21 days. The mesitylene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of mesitylene vapours in air, in the concentration range of 15 mg/m^3 to 310 mg/m^3, for 5 l air samples [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as benzene, toluene, ethylbenzene and p-xylene [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 5 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96.8% (CV = 1%)

Precision: 3.1%

Bias: -7.5%

Overall uncertainty: 13.7%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

MESITYLENE (Trimethylbenzene)	SHEET No 27
CAS No: 108-67-8	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION REPORT: [1]

The desorption efficiency, precision, bias and overall uncertainty data correspond to the data obtained in the validation of 1,2,4-trimethylbenzene. Since mesitylene has the same limit value and is expected to behave in a similar manner during collection in activated charcoal and subsequent desorption with carbon disulphide, the same validation data are assumed for the trimethylbenzenes.

REFERENCES

[1] INSHT. *Determination of Aromatic Hydrocarbons (Benzene, Toluene, Ethylbenzene, p-Xylene, 1,2,4-Trimethylbenzene) in Air. Activated charcoal adsorption / Gas chromatography method* MTA/MA – 030/A92.

OTHER METHODS

CHLOROBENZENE	SHEET No 28
CAS No: 108-90-7	October 2004

LV (8 h): 47 mg/m^3, 10 ppm	LV (short-term): 94 mg/m^3, 20 ppm

SUMMARY OF METHOD

The sample is collected by passing 15 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.3 l/min. The sample can be stored in a refrigerator for 14 days. The chlorobenzene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of chlorobenzene vapours in air, in the concentration range of 4.7 mg/m^3 to 100 mg/m^3, for 15 l air samples [1].

This method also allows the simultaneous determination of other chlorinated aromatic hydrocarbons such as carbon tetrachloride and chloroform [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.3 l/min

Recommended volume: 15 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96% (CV = 2.4%)

Precision: 4.7%

Bias: -3.5%

Overall uncertainty: 12.9%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

CHLOROBENZENE	SHEET No 28
CAS No: 108-90-7	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.3 l/min), the amount of chlorobenzene collected will be 423 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 4.5 mg/m^3 to 95 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 15 l air samples, collected at 0.3 l/min in generated atmospheres, with and without moisture, in the concentration range of 4.5 mg/m^3 to 95 mg/m^3 of chlorobenzene, equivalent to 70 μg/sample and 1420 μg/sample.
The desorption efficiency corresponds to the average of 34 samples in the range of 70 μg/sample to 1800 μg/sample.

REFERENCES

[1] INSHT. *Determination of Chlorinated Hydrocarbons II (Carbon tetrachloride, Chloroform, Chlorobenzene) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA 042/A99.

OTHER METHODS

[2] NIOSH. *Hydrocarbons, Halogenated.* METHOD 1003 [*Activated charcoal tube / Gas chromatography (FID)*].

CYCLOHEXANONE CAS No: 108-94-1	SHEET No 29 October 2004
LV (8 h): 40.8 mg/m^3, 10 ppm	**LV (short-term):** 81.6 mg/m^3, 20 ppm

SUMMARY OF METHOD

The sample is collected by passing 4 l of air through a tube filled with 150 / 75 mg of silica gel using a personal sampling pump at a flow rate of 0.1 l/min. The sample can be stored at room temperature for 14 days. The cyclohexanone is desorbed with ethyl acetate and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of cyclohexanone vapours in air, in the concentration range of 4 mg/m^3 to 80 mg/m^3, for 4 l air samples [1].

This method also allows the simultaneous determination of other ketones such as mesityl oxide [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of silica gel (150 mg / 75 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min

Recommended volume: 4 l

ANALYSIS

Preparation: desorption with 1 ml of ethyl acetate.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 94.8% (CV = 3.6%)

Precision: 4.0%

Bias: -3.4%

Overall uncertainty: 11.4%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

CYCLOHEXANONE	SHEET No 29
CAS No: 108-94-1	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.

For sampling times of 15 minutes, and at the recommended flow rate (0.1 l/min), the amount of cyclohexanone collected will be 122 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 9.8 mg/m^3 to 188 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 2 l air samples, collected at 0.1 l/min in generated atmospheres, with and without moisture, in the concentration range of 9.8 mg/m^3 to 188 mg/m^3 of cyclohexanone, equivalent to 20 μg/sample and 380 μg/sample.

The desorption efficiency corresponds to the average of 52 samples in the range of 16 μg/sample to 56 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **4 l** should be sampled at a flow rate of 0.1 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] INSHT. *Determination of Ketones II (Cyclohexanone, Mesityl oxide) in Air. Silica gel adsorption / Gas chromatography method.* MTA/MA – 052/A02.

OTHER METHODS

[2] NIOSH. *Ketones I.* METHOD 1300 [*Activated charcoal tube / Gas chromatography (FID)*].

[3] OSHA. *Cyclohexanone.* METHOD 1 [*Chromosorb 106 tube / HPLC (UV)*].

[4] INRS. *Ketones I.* SHEET 020 [*Carboxen 1000 tube / Gas chromatography (FID)*].

PHENOL CAS No: 108-95-2	SHEET No 30 October 2004
LV (8 h): 7.8 mg/m^3, 2 ppm	

SUMMARY OF METHOD

The sample is collected by passing 20 l of air through a tube filled with 150 / 75 mg of silica gel using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 14 days. The phenol is desorbed with acetone and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of phenol vapours in air, in the concentration range of 0.78 mg/m^3 to 15 mg/m^3, for 20 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of silica gel (150 mg / 75 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 20 l

ANALYSIS

Preparation: desorption with 1 ml of acetone.

Analytical technique: gas chromatography with flame ionisation detector and 2 m glass column with 10% Carbowax 20M or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 99.2% (CV = 3.3%)

Precision: 4.8%

Bias: -1.6%

Overall uncertainty: 11.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

PHENOL	SHEET No 30
CAS No: 108-95-2	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 1.8 mg/m^3 to 43 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 10 l air samples, generated using a system for adding phenol to tubes, over which air with 50% humidity is also passed. The tested concentration range is 1.8 mg/m^3 to 43 mg/m^3 of phenol, equivalent to 18 μg/sample and 430 μg/sample.

The desorption efficiency corresponds to the average of 21 samples in the range of 17 μg/sample to 400 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **20 l** should be sampled at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] INSHT. *Determination of Phenol in Air. Silica gel adsorption / Gas chromatography method.* MTA/MA – 040/A98.

OTHER METHODS

[2] DFG. *Phenol.* Analyses of Hazardous Substances in Air. Vol. 3 p. 99 [*Silica gel tube / Gas chromatography (FID)*].

[3] NIOSH. *Cresol (all isomers) and Phenol.* METHOD 2546 [*XAD-7 tube / Gas chromatography (FID)*].

[4] OSHA. *Phenol and Cresol.* METHOD 32 [*XAD-7 tube / HPLC (UV)*].

TETRAHYDROFURAN CAS No: 109-99-9	SHEET No 31 October 2004
LV (8 h): 150 mg/m^3, 50 ppm	**LV (short-term):** 300 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 12 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored at room temperature for 14 days. The tetrahydrofuran is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of tetrahydrofuran vapours in air, in the concentration range of 15 mg/m^3 to 300 mg/m^3, for 12 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 12 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 14 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96.4% (CV = 1%)

Precision: 1.1%

Bias: -6.9%

Overall uncertainty: 9.1%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

TETRAHYDROFURAN	SHEET No 31
CAS No: 109-99-9	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of tetrahydrofuran collected will be 900 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 13 mg/m^3 to 270 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 12 l air samples, collected at 0.2 l/min in generated atmospheres, with and without moisture, in the concentration range of 13 mg/m^3 to 270 mg/m^3 of tetrahydrofuran, equivalent to 160 μg/sample and 3200 μg/sample.
The desorption efficiency corresponds to the average of 24 samples in the range of 16 μg/sample to 3500 μg/sample.

REFERENCES

[1] INSHT. *Determination of Tetrahydrofuran in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 049/A01.

OTHER METHODS

[2] DFG. *Tetrahydrofuran.* Analyses of Hazardous Substances in Air. Volume 3 [*Activated charcoal tube / Gas chromatography (FID)*].

[3] NIOSH. *Tetrahydrofuran.* METHOD 1609 [*Activated charcoal tube / Gas chromatography (FID)*].

5-METHYL-2-HEXANONE (Methyl isoamyl ketone)

CAS No: 110-12-3

SHEET No 32

October 2004

LV (8 h): 95 mg/m^3, 20 ppm

SUMMARY OF METHOD

The sample is collected by passing 10 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The 5-methyl-2-hexanone is desorbed with a solution of 1% dimethylformamide in carbon disulphide (1:99) and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The applicability of the method has not been confirmed [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide containing 1% (v/v) dimethylformamide.

Analytical technique: gas chromatography with flame ionisation detector and DB-WAX capillary column or similar.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 10 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96.2% (CV = 1.70%)

Precision: no data available

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

5-METHYL-2-HEXANONE (Methyl isoamyl ketone)	SHEET No 32
CAS No: 110-12-3	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method is classed as partially validated by OSHA.

The desorption efficiency given in the method corresponds to the average of 20 samples in the range of 230 μg/sample to 4570 μg/sample.

A stability study was conducted by adding 2286 μg of 5-methyl-2-hexanone to 12 tubes and, after 2 hours, passing 10 l of air over them, with a relative humidity of 80%, at a flow rate of 0.2 l/min. They were stored for 10 days at either room temperature (6 tubes) or refrigerated at 0ºC (6 tubes). Recovery was 59.5% for tubes stored at room temperature and 95.4% for the refrigerated tubes.

The data provided in the above method are inadequate and insufficiently conclusive for the method to be evaluated.

REFERENCES

[1] OSHA. *MIAK (Methyl Isoamyl Ketone).* METHOD PV-2042.

OTHER METHODS

[2] OSHA. *Chemical Sampling Information. Methyl Isoamyl Ketone*. IMIS: 1776.

2-HEPTANONE (Methyl amyl ketone)

CAS No: 110-43-0

SHEET No 33

October 2004

LV (8 h): 238 mg/m^3, 50 ppm

LV (short-term): 475 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing a quantity of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The 2-heptanone is desorbed with 1 ml of carbon disulphide containing 1% (1:99) methanol and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 2-heptanone in air, in the concentration range of 23.8 mg/m^3 to 500 mg/m^3, for sample volumes ranging from 18 l to 80 l of air [1].

This method also allows the simultaneous determination of other ketones such as ethyl butyl ketone, mesityl oxide, etc. [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 18 l to 80 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide containing 1% (1:99) methanol.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or similar.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 82% (CV = 4.2%)

Precision: 5.8%

Bias: 2.8%

Overall uncertainty: 14.4%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

2-HEPTANONE (Methyl amyl ketone) CAS No: 110-43-0	SHEET No 33 October 2004

OTHER INFORMATION OF INTEREST

The applicability of the method for measuring concentrations comparable with the short-term LV has not been confirmed.

For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 2-heptanone collected will be 1425 μg/sample, which is outside the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 197 mg/m^3 to 925 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture, at a concentration of 197 mg/m^3 to 925 mg/m^3 of 2-heptanone, for 10 l air samples, equivalent to 1970 μg/sample and 9250 μg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 2320 μg/sample to 9300 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **80 l** should be sampled for concentrations of 0.1 LV (24 mg/m^3) to 0.5 LV (119 mg/m^3) and at least **18 l** for concentrations of 0.5 LV (119 mg/m^3) to 2 LV (476 mg/m^3) at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Ketones II.* METHOD 1301.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 15.* DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

PIPERAZINE CAS No: 110-85-0	SHEET No 34 October 2004
LV (8 h): 0.1 mg/m^3	**LV (short-term):** 0.3 mg/m^3

SUMMARY OF METHOD

The sample is collected by passing 10 l of air through a tube filled with 80 / 40 mg of XAD-2 impregnated with 10% 1-naphthyl isocyanate using a personal sampling pump at a flow rate of 0.1 l/min. The piperazine is desorbed with dimethylformamide and the resulting solution is analysed in a high-performance liquid chromatograph equipped with an ultraviolet detector [1].

SCOPE

The applicability of the method has not been confirmed [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: tube filled with 80 / 40 mg of XAD-2 impregnated with 10% (w/w) 1-naphthyl isocyanate

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min

Recommended volume: 10 l

ANALYSIS

Preparation: desorption with dimethylformamide.

Analytical technique: high-performance liquid chromatography with ultraviolet detector.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: no data available

Precision: no data available

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: high

PIPERAZINE CAS No: 110-85-0	SHEET No 34 October 2004

OTHER INFORMATION OF INTEREST

REFERENCES

[1] OSHA. *Chemical Sampling Information. Piperazine*. IMIS: P250.

OTHER METHODS

[2] Skarping G. *Determination of piperazines in the working atmosphere and in human urine using derivatization and capillary gas chromatography with nitrogen- and mass-selective detection*. J. Chromatogr. 1986; 370: 245-258.

2-BUTOXYETHANOL (Butyl cellosolve) CAS No: 111-76-2	SHEET No 35 October 2004
LV (8 h): 98 mg/m^3, 20 ppm	**LV (short-term):** 246 mg/m^3, 50 ppm

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored at room temperature for 15 days. The 2-butoxyethanol is desorbed with dichloromethane containing 5% methanol and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 2-butoxyethanol in air, in the concentration range of 9.8 mg/m^3 to 200 mg/m^3, for sample volumes ranging from 12 l to 48 l of air [1].

This method also allows the simultaneous determination of 2-butoxyethyl acetate [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 12 l to 48 l

ANALYSIS

Preparation: desorption with 1 ml of dichloromethane containing 5% (v/v) methanol.

Analytical technique: gas chromatography with flame ionisation detector and NUKOL capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 99% (CV = 0.6%)

Precision: 0.6%

Bias: -2.0%

Overall uncertainty: 3.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

2-BUTOXYETHANOL (Butyl cellosolve) CAS No: 111-76-2	SHEET No 35 October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 2-butoxyethanol collected will be 738 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration of 96 mg/m^3 (1 LV). This value coincides with the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 12 l air samples, collected at 0.2 l/min in generated atmospheres, with moisture, at a concentration of 96 mg/m^3, which is equivalent to 1152 μg/sample.
The desorption efficiency corresponds to the average of 18 samples in the range of 570 μg/sample to 2280 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the range of 55 μg/sample to 2280 μg/sample in which the method was studied.

To do this, at least **48 l** should be sampled for air concentrations of 0.1 LV (1 mg/m^3) to 0.5 LV (49 mg/m^3) and at least **12 l** for air concentrations of 0.5 LV (49 mg/m^3) to 2 LV (196 mg/m^3) at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation would allow the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] OSHA. *2-Butoxyethanol / 2-Butoxyethyl Acetate.* METHOD 83.

OTHER METHODS

[2] NIOSH. *Alcohols IV.* METHOD 1403 [*Activated charcoal tube / Gas chromatography (FID)*].

2-BUTOXYETHYL ACETATE

CAS No: 112-07-2

SHEET No 36

October 2004

LV (8 h): 133 mg/m^3, 20 ppm

LV (short-term): 333 mg/m^3, 50 ppm

SUMMARY OF METHOD

The sample is collected by passing 40 l of air through a tube filled with 700 / 300 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 3 weeks. The 2-butoxyethyl acetate is desorbed with diethylether and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 2-butoxyethyl acetate in air, in the concentration range of 13 mg/m^3 to 266 mg/m^3, for 40 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: activated charcoal tube (700 mg / 300 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 40 l

ANALYSIS

Preparation: desorption with 6 ml of diethylether.

Analytical technique: gas chromatography with flame ionisation detector and OV1 capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

After sampling, samples should be refrigerated as soon as possible to reduce hydrolysis and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 90%

Precision: 10.1%

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

2-BUTOXYETHYL ACETATE	SHEET No 36
CAS No: 112-07-2	October 2004

OTHER INFORMATION OF INTEREST

The method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 2-butoxyethyl acetate collected will be 999 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 5 mg/m^3 to 300 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision shown in the sheet corresponds to samples collected in generated atmospheres without moisture, at a concentration of 5 mg/m^3 to 300 mg/m^3 of 2-butoxyethyl acetate, for 40 l air samples, equivalent to 200 μg/sample and 1200 μg/sample.
Desorption efficiency is independent of the concentration in the measuring range.
The sample storage study is only mentioned as no data is available.
No data is available with which to calculate the bias.

REFERENCES

[1] DFG. *2-Butoxyethyl acetate.* ANALYSES OF HAZARDOUS SUBSTANCES IN AIR. Vol. 2 p. 73.

OTHER METHODS

[2] OSHA. *2-Butoxyethanol / 2-Butoxyethyl Acetate.* METHOD 83 [*Activated charcoal tube / Gas chromatography (FID)*].

DIMETHYLETHER CAS No: 115-10-6	SHEET No 37 October 2004
LV (8 h): 1920 mg/m^3, 1000 ppm	

SUMMARY OF METHOD

The sample can be collected by passing 1 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.05 l/min. The dimethylether is desorbed with 1 ml of carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of dimethylether in air, in the concentration range of 190 mg/m^3 to 3850 mg/m^3, for 1 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.05 l/min

Recommended volume: 1 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and SE-30 capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 100% (CV = 1.7%)

Precision: 1.2%

Bias: -5.2%

Overall uncertainty: 7.6%

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: medium

DIMETHYLETHER	SHEET No 37
CAS No: 115-10-6	October 2004

OTHER INFORMATION OF INTEREST

The desorption efficiency, precision and bias data correspond to the data obtained in the validation of **DIETHYLETHER**.

ADAPTATION OF THE METHOD

Assuming both ethers behave similarly in activated charcoal, and in order to allow the use of the diethylether validation data, **1 l** should be sampled, for concentrations of 0.1 LV (192 mg/m^3) and 2 LV (3840 mg/m^3), equivalent to 192 µg/sample and 3840 µg/sample. These amounts correspond to those for validating the diethylether method.

NOTES

Since this is a gas, the above modifications should be checked.

REFERENCES

[1] INSHT. *Determination of Ethers I (Diethylether, Diisopropyl ether, Methyl tert-butyl ether) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 047/A01.

OTHER METHODS

1,2,4-TRICHLOROBENZENE

CAS No: 120-82-1

SHEET No 38

October 2004

LV (8 h): 15.1 mg/m^3, 2 ppm

LV (short-term): 37.8 mg/m^3, 5 ppm

SUMMARY OF METHOD

The sample is collected by passing 10 l of air through a two-part sampler, composed of a 13 mm PTFE filter on a stainless steel support and a tube filled with 100 / 50 mg of XAD-2, using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored, at room temperature and protected from light, for 13 days. The 1,2,4-trichlorobenzene is desorbed with hexane and the resulting solution is analysed in a gas chromatograph equipped with an electron-capture detector.

SCOPE

The method is applicable to the determination of 1,2,4-trichlorobenzene in air, in the concentration range of 1.5 mg/m^3 to 30 mg/m^3, for 10 l air samples [1].

This method also allows the simultaneous determination of other polychlorobenzenes such as 1,2,4,5-tetrachlorobenzene and pentachlorobenzene [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: 13 mm PTFE filter + XAD-2 adsorbent tube (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l

ANALYSIS

Preparation: separate desorption of the two parts with 2 ml of hexane, with ultrasonic agitation for 30 minutes.

Analytical technique: gas chromatography, with nickel 63 electron-capture detector, and 2 m nickel column containing 10% Carbowax 20M or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Once sampling has been completed, the filter should be separated from the tube and both components should be protected from light. Samples do not display any loss when stored at room temperature and analysed within 13 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 90.8% (CV: no data available)

Precision: 9.3%

Bias: -4.3%

Overall uncertainty: 22.9%

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: medium

1,2,4-TRICHLOROBENZENE	SHEET No 38
CAS No: 120-82-1	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 1,2,4-trichlorobenzene collected will be 203 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 0.002 mg/m^3 to 100 mg/m^3. This range includes the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture, at a concentration of 0.002 mg/m^3 to 100 mg/m^3 of 1,2,4-trichlorobenzene, for 10 l air samples, equivalent to 2 μg/sample and 1000 μg/sample.
The desorption efficiency corresponds to the average of samples in the range of 0.02 μg/sample to 500 μg/sample.

REFERENCES

[1] NIOSH. *Polychlorobenzenes.* METHOD 5517.

OTHER METHODS

TRIETHYLAMINE CAS No: 121-44-8	SHEET No 39 October 2004
LV (8 h): 8.4 mg/m^3, 2 ppm	**LV (short-term):** 12.6 mg/m^3, 3 ppm

SUMMARY OF METHOD

The sample is collected by passing 50 l of air through a tube filled with 80 / 40 mg of XAD-7 impregnated with 10% phosphoric acid, using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored at room temperature for 15 days. The triethylamine is desorbed with a 50% (v/v) water / methanol solution for 30 minutes. An aliquot is alkalised with a 25% (v/v) solution of 1N NaOH / methanol and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of triethylamine in air, in the concentration range of 0.84 mg/m^3 to 16.8 mg/m^3, in 50 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: tube filled with 80 / 40 mg of XAD-7 impregnated with 10% phosphoric acid

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 50 l

ANALYSIS

Preparation: desorption with 1 ml of 1:1 water / methanol (v/v) for 30 minutes, after which a 0.5 ml aliquot is removed and alkalised with 0.5 ml of a 1:4 1N NaOH / methanol solution.

Analytical technique: gas chromatography with flame ionisation detector and Stabilwax DB capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 99.9% (CV = 1.5%)

Precision: 1.6%

Bias: +0.9%

Overall uncertainty: 4.1%

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: medium

TRIETHYLAMINE	SHEET No 39
CAS No: 121-44-8	October 2004

OTHER INFORMATION OF INTEREST

The applicability of the method for measuring concentrations comparable with the short-term LV has not been confirmed.

For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of triethylamine collected will be 38 μg/sample, which is outside the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is partially validated. The precision and bias shown in the sheet correspond to samples spiked with 828 μg of triethylamine, over which 20 l of air with 86% humidity is circulated, at a flow rate of 0.2 l/min, this being equivalent to 41.8 mg/m^3.

This value is outside the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The desorption efficiency corresponds to the average of 24 samples in the range of 41 μg/sample to 828 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the range of 41 μg/sample to 828 μg/sample in which the method was studied.

To do this, at least **50 l** should be sampled at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation would allow the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] OSHA. *Triethylamine / Trimethylamine.* METHOD PV 2060.

OTHER METHODS

[2] DFG. *Dimethylethylamine / Triethylamine.* Analyses of Hazardous Substances in Air. Vol. 1 p. 165. [*1 g of silica gel / Gas chromatography (FID)*].

ISOPENTYLACETATE (Isoamyl acetate) **CAS No: 123-92-2**	**SHEET No 40** **October 2004**
LV (8 h): 270 mg/m^3, 20 ppm	**LV (short-term):** 540 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 2 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min. The sample can be stored at room temperature for 15 days. The isopentylacetate is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of isopentylacetate in air, in the concentration range of 27 mg/m^3 to 540 mg/m^3, for 2 l air samples [1].

This method also allows the simultaneous determination of other esters such as n-propyl acetate and n-amyl acetate [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min

Recommended volume: 2 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with FFAP capillary column, or any other capable of separating the analytes of interest, and flame ionisation detector.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 97.6% (CV = 2.3%)

Precision: 2.6%

Bias: -3.4%

Overall uncertainty: 8.6%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

ISOPENTYLACETATE (Isoamyl acetate)	SHEET No 40
CAS No: 123-92-2	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the recommended flow rate (0.1 l/min), the amount of isopentylacetate collected will be 810 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 24 mg/m^3 to 550 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 2 l air samples, collected at 0.1 l/min in generated atmospheres, with and without moisture, in the concentration range of 24 mg/m^3 to 550 mg/m^3 of isopentylacetate, equivalent to 48 μg/sample and 1100 μg/sample.
The desorption efficiency corresponds to the average of 24 samples in the range of 44 μg/sample to 1020 μg/sample.

REFERENCES

[1] INSHT. *Determination of Esters III (n-Propyl acetate, Isoamyl acetate, n-Amyl acetate) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 041/A99.

OTHER METHODS

[2] NIOSH. *Esters I.* METHOD 1450 [*Activated charcoal tube / Gas chromatography (FID)*].

DIMETHYLAMINE CAS No: 124-40-3	SHEET No 41 October 2004
LV (8 h): 3.8 mg/m^3, 2 ppm	**LV (short-term):** 9.4 mg/m^3, 5 ppm

SUMMARY OF METHOD

The sample is collected by passing 50 l of air through a tube filled with 150 / 75 mg of silica gel using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored at room temperature for 6 days. The dimethylamine is desorbed with 0.1M sulphuric acid in a 10% (v/v) aqueous methanol solution. An aliquot is alkalised with 0.3M KOH and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is not applicable in the range 0.1 LV to ≈ 2 LV. (See "Other information of interest").

The method is applicable to the determination of dimethylamine in air, in the concentration range of 7.3 mg/m^3 (2 LV) to 30.5 mg/m^3 (8 LV), for 50 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of silica gel (150 mg / 75 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 50 l

ANALYSIS

Preparation: desorption with 1 ml of 0.1M sulphuric acid in 10% (v/v) aqueous methanol solution; once desorbed, a 0.5 ml aliquot is removed and alkalised with 0.5 ml of 0.3M KOH.

Analytical technique: gas chromatography with flame ionisation detector and 1.8 m column with 4% Carbowax 20M + 0.8% KOH or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 6 days of collection [2].

METHOD EVALUATION DATA

Desorption efficiency: 91.6% (CV = 3%)

Precision: 5.2%

Bias: -2.9%

Overall uncertainty: 13.3%

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: medium

DIMETHYLAMINE	SHEET No 41
CAS No: 124-40-3	October 2004

OTHER INFORMATION OF INTEREST

The method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of dimethylamine collected will be 470 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 7.3 mg/m^3 to 30.5 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture, at a concentration of 7.3 mg/m^3 to 30.5 mg/m^3 of dimethylamine, for 50 l air samples, equivalent to 360 μg/sample and 1525 μg/sample.
The desorption efficiency corresponds to the average of 18 samples in the range of 408 μg/sample to 1670 μg/sample.
It has also been confirmed that in 48 l samples, collected at 1.1 l/min at a concentration of 36 mg/m^3, no dimethylamine was found in the posterior part of the adsorbent tube.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it would need to be adapted to the current scope of interest defined in relation to the LV.
The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **1000 l** would need to be sampled for concentrations of 0.1 LV (0.38 mg/m^3) to 0.5 LV (1.9 mg/m^3) and at least **240 l** for concentrations of 0.5 LV (1.9 mg/m^3) to 2 LV (7.6 mg/m^3) at a flow rate of 0.2 l/min, which means its adaptation is unfeasible.
It is therefore not possible to relate the precision and bias values obtained in the validation to the current concentration range of interest.

NOTE

This method could be used in the application range of 0.2 LV (0.76 mg/m^3) to 1 LV (3.6 mg/m^3) if 480 l were sampled at 1 l/min but, as this is a gas, the breakthrough volume should at least be confirmed.

REFERENCES

[1] NIOSH. *Amines, Aliphatic.* METHOD 2010.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 142.* DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

[3] OSHA. Dimethylamine. METHOD 34 [*XAD-7 with 10% NBD chloride (not commercially available) / HPLC*].

N,N-DIMETHYLACETAMIDE CAS No: 127-19-5	SHEET No 42 October 2004
LV (8 h): 36 mg/m^3, 10 ppm	**LV (short-term):** 72 mg/m^3, 20 ppm

SUMMARY OF METHOD

The sample is collected by passing a quantity of air through a tube filled with 150 / 75 mg of silica gel using a personal sampling pump at a flow rate of 1 l/min. The N,N-dimethylacetamide is desorbed with methanol and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of N,N-dimethylacetamide in air, in the concentration range of 3.6 mg/m^3 to 72 mg/m^3, for air samples of 50 l to 240 l [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of silica gel (150 mg / 75 mg)

Sampling pump: personal type G

Recommended flow rate: 1 l/min

Recommended volume: 50 l to 240 l

ANALYSIS

Preparation: desorption with 1 ml of methanol and ultrasonic agitation for 1 h.

Analytical technique: gas chromatography with flame ionisation detector and column with 10% UCON 50-HB-5100 + 2% KOH or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples may remain stable for 5 days (temperature not specified).

METHOD EVALUATION DATA

Desorption efficiency: 92.5% (CV = 4.1%)

Precision: 6.8%

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

N,N-DIMETHYLACETAMIDE	SHEET No 42
CAS No: 127-19-5	October 2004

OTHER INFORMATION OF INTEREST

The method can be used to measure concentrations comparable with the short-term LV.

For sampling times of 15 minutes, and at the recommended flow rate (1 l/min), the amount of N,N-dimethylacetamide collected will be 1080 μg/sample, which lies within the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 18 mg/m^3 to 105 mg/m^3. This range only partially coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture at a concentration of 18 mg/m^3 to 105 mg/m^3 of N,N-dimethylacetamide, for 45 l air samples, collected at 0.88 l/min, equivalent to 810 μg/sample and 4750 μg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 943 μg/sample to 3770 μg/sample.

In addition, the breakthrough volume calculated at a flow rate of 0.876 l/min and a concentration of 106 mg/m^3 was 46 l, which is equivalent to 22000 μg per 150 mg of silica gel.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **240 l** should be sampled for concentrations of 0.1 LV (3.6 mg/m^3) to 0.5 LV (18 mg/m^3) and at least **50 l** for concentrations of 0.5 LV (18 mg/m^3) to 2 LV (72 mg/m^3) at a flow rate of 1 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Dimethylacetamide.* METHOD 2004.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 254.* DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

N-BUTYLACRYLATE CAS No: 141-32-2	SHEET No 43 October 2004
LV (8 h): 11 mg/m^3, 2 ppm	**LV (short-term):** 53 mg/m^3, 10 ppm

SUMMARY OF METHOD

The sample is collected by passing 60 l of air through a tube filled with 100 / 50 mg of activated charcoal impregnated with 10% 4-*tert*-butylcatechol (TBC), using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored at room temperature for 10 days. The n-butylacrylate is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of n-butylacrylate in air, in the concentration range of 1.1 mg/m^3 to 22 mg/m^3, for 60 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: tube filled with 100 / 50 mg of activated charcoal impregnated with 10% 4-*tert*-butylcatechol

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 60 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and DX-4 capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 10 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 100% (CV = 3.1%)

Precision: 1.3%

Bias: - 4.7%

Overall uncertainty: 7.3%

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: medium

N-BUTYLACRYLATE	SHEET No 43
CAS No: 141-32-2	October 2004

OTHER INFORMATION OF INTEREST

The applicability of the method for measuring concentrations comparable with the short-term LV has not been confirmed.

For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of n-butylacrylate collected will be 159 μg/sample, which is outside the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is partially validated. The precision and bias shown in the sheet correspond to samples spiked with 674 μg of n-butylacrylate, over which is circulated 12 l of air with 80% humidity is circulated at a flow rate of 0.2 l/min, this being equivalent to 56 mg/m^3.

This value is outside the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The desorption efficiency corresponds to the average of 20 samples in the range of 67 μg/sample to 1348 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the range of 67 μg/sample to 1348 μg/sample in which the method was studied.

To do this, at least **60 l** should be sampled at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] OSHA. *Butyl Acrylate.* METHOD PV 2011.

OTHER METHODS

[2] DFG. *Acrylates (Methyl acrylate, Ethyl acrylate, Butyl acrylate)* Analyses of Hazardous Substances in Air**.** Vol. 3 p. 35. [*Activated charcoal tube / Gas chromatography (FID)*].

N-HEPTANE CAS No: 142-82-5	SHEET No 44 October 2004

LV (8 h): 2085 mg/m^3, 500 ppm

SUMMARY OF METHOD

The sample is collected by passing 1 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.05 l/min. The sample can be stored at room temperature for 15 days. The n-heptane is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of n-heptane in air, in the concentration range of 208 mg/m^3 to 4170 mg/m^3, for 1 l air samples [1].

This method also allows the simultaneous determination of other hydrocarbons such as n-hexane, n-octane and n-nonane [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.05 l/min

Recommended volume: 1 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 101.4% (CV = 2.2%)

Precision: 3.2%

Bias: 2.6%

Overall uncertainty: 9%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

N-HEPTANE	SHEET No 44
CAS No: 142-82-5	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 134 mg/m^3 to 2955 mg/m^3. This range **does not** coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 2 l air samples, collected at 0.1 l/min in generated atmospheres, with and without moisture, in the concentration range of 134 mg/m^3 to 2955 mg/m^3 of n-heptane, equivalent to 268 μg/sample and 5900 μg/sample.

The desorption efficiency corresponds to the average of 12 samples in the range of 220 μg/sample to 4830 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **1 l** should be sampled at a flow rate of 0.05 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] INST. *Determination of Aliphatic Hydrocarbons (Hexane, Heptane, Octane, Nonane) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 029/A92.

OTHER METHODS

[2] NIOSH. *Hydrocarbons, 36 - 126ºC BP.* METHOD 1500 [*Activated charcoal tube / Gas chromatography (FID)*].

1,2,3-TRIMETHYLBENZENE

CAS No: 526-73-8

SHEET No 45

October 2004

LV (8 h): 100 mg/m^3, 20 ppm

SUMMARY OF METHOD

The sample is collected by passing 8 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 21 days. The 1,2,3-trimethylbenzene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 1,2,3-trimethylbenzene vapours in air, in the concentration range of 10 mg/m^3 to 200 mg/m^3, for 8 l air samples [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as benzene, toluene, ethylbenzene, p-xylene and 1,2,4-trimethylbenzene [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 8 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96.8% (CV = 1%)

Precision: 3.1%

Bias: -7.5%

Overall uncertainty: 13.7%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

1,2,3-TRIMETHYLBENZENE	SHEET No 45
CAS No: 526-73-8	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION REPORT: [1]

The desorption efficiency, precision, bias and overall uncertainty data correspond to the data obtained in the validation of 1,2,4-trimethylbenzene. Since 1,2,3-trimethylbenzene has the same limit value and is expected to behave in a similar manner during collection in activated charcoal and subsequent desorption with carbon disulphide, the same validation data are assumed for both trimethylbenzenes.

REFERENCES

[1] INSHT. *Determination of Aromatic Hydrocarbons (Benzene, Toluene, Ethylbenzene, p-Xylene, 1,2,4-Trimethylbenzene) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 030/A92.

OTHER METHODS

5-METHYL-3-HEPTANONE

CAS No: 541-85-5

SHEET No 46

October 2004

LV (8 h): 53 mg/m^3, 10 ppm

LV (short-term): 107 mg/m^3, 20 ppm

SUMMARY OF METHOD

The sample is collected by passing a quantity of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The 5-methyl-3-heptanone is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 5-methyl-3-heptanone vapours in air, in the concentration range of 5.3 mg/m^3 to 106 mg/m^3, for air samples of 24 l to 96 l [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 24 l to 96 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with FFAP capillary column, or any other capable of separating the analytes of interest, and flame ionisation detector.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 89.8% (CV = 2.6%)

Precision: 8.8%

Bias: 15.2%

Overall uncertainty: 32.8%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

5-METHYL-3-HEPTANONE	SHEET No 46
CAS No: 541-85-5	October 2004

OTHER INFORMATION OF INTEREST

The applicability of the method for measuring concentrations comparable with the short-term LV has not been confirmed.

For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 5-methyl-3-heptanone collected will be 318 μg/sample, which is outside the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 57.5 mg/m^3 to 272 mg/m^3. This range only partially coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture, at a concentration of 57.5 mg/m^3 to 272 mg/m^3 of 5-methyl-3-heptanone, for 10 l air samples, equivalent to 575 μg/sample and 2720 μg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 650 μg/sample to 2600 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **96 l** should be sampled for concentrations of 0.1 LV (5.3 mg/m^3) to 0.5 LV (26.5 mg/m^3) and at least **24 l** for concentrations of 0.5 LV (26.5 mg/m^3) to 2 LV (106 mg/m^3) at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Ketones II.* METHOD 1301.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 13.* DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

1-METHYLBUTYLACETATE (sec-Amyl acetate)

CAS No: 626-38-0

SHEET No 47

October 2004

LV (8 h): 270 mg/m^3, 20 ppm

LV (short-term): 540 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing a quantity of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The 1-methylbutylacetate is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 1-methylbutylacetate in air, in the concentration range of 27 mg/m^3 to 540 mg/m^3, for air samples of 24 l to 96 l [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 24 l to 96 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: 93.2% (CV = 4.6%)

Precision: 5.4%

Bias: -7%

Overall uncertainty: 17.8%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

1-METHYLBUTYLACETATE (sec-Amyl acetate) CAS No: 626-38-0	SHEET No 47 October 2004

OTHER INFORMATION OF INTEREST

The applicability of the method for measuring concentrations comparable with the short-term LV has not been confirmed.

For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of 1-methylbutylacetate collected will be 1620 μg/sample, which is outside the application range for the method.

METHOD VALIDATION INFORMATION: [1] and [2]

The method [1] is validated for the concentration range of 340 mg/m^3 to 1460 mg/m^3. This range only partially coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to samples collected in generated atmospheres without moisture, at a concentration of 340 mg/m^3 to 1460 mg/m^3 of 1-methylbutylacetate, for 10 l air samples, equivalent to 3400 μg/sample and 14600 μg/sample.

The desorption efficiency corresponds to the average of 18 samples in the range of 3300 μg/sample to 13000 μg/sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **96 l** should be sampled for concentrations of 0.1 LV (27 mg/m^3) to 0.5 LV (135 mg/m^3) and at least **24 l** for concentrations of 0.5 LV (135 mg/m^3) to 2 LV (540 mg/m^3) at a flow rate of 0.1 l/min to 0.2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] NIOSH. *Esters I.* METHOD 14502.

[2] DOCUMENTATION OF THE NIOSH VALIDATION TESTS. *S 31*. DHEW (NIOSH) Publication No 77-185.

OTHER METHODS

[3] INST. *Determination of Esters III (n-Propyl acetate, Isoamyl acetate, n-Amyl acetate) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 041/A99.

PENTYLACETATE (n-Amyl acetate) CAS No: 628-63-7	SHEET No 48 October 2004
LV (8 h): 270 mg/m^3, 20 ppm	**LV (short-term):** 540 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 2 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min. The sample can be stored at room temperature for 15 days. The pentylacetate is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of pentylacetate in air, in the concentration range of 27 mg/m^3 to 540 mg/m^3, for 2 l air samples [1].

This method also allows the simultaneous determination of other esters such as n-propyl acetate and iso-pentylacetate [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min

Recommended volume: 2 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96.5% (CV = 1.8%)

Precision: 2.5%

Bias: -5.7%

Overall uncertainty: 10.7%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

PENTYLACETATE (n-Amyl acetate)	SHEET No 48
CAS No: 628-63-7	October 2004

OTHER INFORMATION OF INTEREST

The method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the recommended flow rate (0.1 l/min), the amount of pentylacetate collected will be 810 μg/sample, which is outside the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration range of 27 mg/m^3 to 540 mg/m^3. This range coincides with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision and bias shown in the sheet correspond to 2 l air samples, collected in generated atmospheres, with and without moisture, in the concentration range of 27 mg/m^3 to 540 mg/m^3 of pentylacetate, equivalent to 54 μg/sample and 1080 μg/sample.
The desorption efficiency corresponds to the average of 24 samples in the range of 44 μg/sample to 1020 μg/sample.

REFERENCES

[1] INST. *Determination of Esters III (n-Propyl acetate, Isoamyl acetate, n-Amyl acetate) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 041/A99.

OTHER METHODS

[2] NIOSH. *Esters I.* METHOD 14502 [*Activated charcoal tube / Gas chromatography (FID)*].

3-PENTYLACETATE CAS No: 620-11-1	SHEET No 49 October 2004
LV (8 h): 270 mg/m^3, 20 ppm	**LV (short-term):** 540 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 2 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min. The sample can be stored at room temperature for 15 days. The 3-pentylacetate is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 3-pentylacetate in air, in the concentration range of 27 mg/m^3 to 540 mg/m^3, for 2 l air samples [1].

This method also allows the simultaneous determination of other esters such as n-propyl acetate and iso-pentylacetate [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min

Recommended volume: 2 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96.5% (CV = 1.8%)

Precision: 2.5%

Bias: -5.7%

Overall uncertainty: 10.7%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

3-PENTYLACETATE	SHEET No 49
CAS No: 620-11-1	October 2004

OTHER INFORMATION OF INTEREST

The method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the recommended flow rate (0.1 l/min), the amount of 3-pentylacetate collected will be 810 μg/sample, which is outside the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The desorption efficiency, precision, bias and overall uncertainty data correspond to the data obtained in the validation of pentylacetate. Since 3-pentylacetate has the same limit value, and assuming the same behaviour during collection in activated charcoal and subsequent desorption with carbon disulphide, the same validation data are assumed for both acetates.

REFERENCES

[1] INST. *Determination of Esters III (n-Propyl acetate, Isoamyl acetate, n-Amyl acetate) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 041/A99.

OTHER METHODS

[2] NIOSH. *Esters I.* METHOD 14502. [*Activated charcoal tube / Gas chromatography (FID)*].

tert-AMYLACETATE CAS No: 625-16-1	SHEET No 50 October 2004
LV (8 h): 270 mg/m^3, 20 ppm	**LV (short-term):** 540 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 2 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min. The sample can be stored at room temperature for 15 days. The tert-amyl acetate is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of tert-amyl acetate in air, in the concentration range of 27 mg/m^3 to 540 mg/m^3, for 2 l air samples [1].

This method also allows the simultaneous determination of other esters such as n-propyl acetate and iso-pentylacetate [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min

Recommended volume: 2 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 96.5% (CV = 1.8%)

Precision: 2.5%

Bias: -5.7%

Overall uncertainty: 10.7%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

tert-AMYLACETATE CAS No: 625-16-1	SHEET No 50 October 2004

OTHER INFORMATION OF INTEREST

The method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the recommended flow rate (0.1 l/min), the amount of tert-amyl acetate collected will be 810 μg/sample, which is outside the application range for the method.

METHOD VALIDATION INFORMATION: [1]

The desorption efficiency, precision, bias and overall uncertainty data correspond to the data obtained in the validation of pentylacetate. Since tert-amyl acetate has the same limit value, and assuming the same behaviour during collection in activated charcoal and subsequent desorption with carbon disulphide, the same validation data are assumed for both acetates.

REFERENCES

[1] INST. *Determination of Esters III (n-Propyl acetate, Isoamyl acetate, n-Amyl acetate) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 041/A99.

OTHER METHODS

[2] NIOSH. *Esters I.* METHOD 14502 [*Activated charcoal tube / Gas chromatography (FID)*].

XYLENES (Mixed isomers)

CAS No: 1330-20-7

SHEET No 51

October 2004

LV (8 h): 221 mg/m^3, 20 ppm

LV (short-term): 442 mg/m^3, 100 ppm

SUMMARY OF METHOD

The sample is collected by passing 10 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored in a refrigerator for 21 days. The xylene is desorbed with carbon disulphide and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of xylene vapours in air, in the concentration range of 22 mg/m^3 to 450 mg/m^3, for 10 l air samples [1].

This method also allows the simultaneous determination of other aromatic hydrocarbons such as ethylbenzene, benzene, toluene and 1,2,4-trimethylbenzene [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l

ANALYSIS

Preparation: desorption with 1 ml of carbon disulphide.

Analytical technique: gas chromatography with flame ionisation detector and FFAP capillary column or any other capable of separating the analytes of interest.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 98.5% (CV = 1%)

Precision: 1.3%

Bias: -7.6%

Overall uncertainty: 10.2%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

XYLENES (Mixed isomers)	SHEET No 51
CAS No: 1330-20-7	October 2004

OTHER INFORMATION OF INTEREST

This method can be used to measure concentrations comparable with the short-term LV.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.2 l/min), the amount of xylene collected will be 1326 μg/sample, which lies within the application range for the method.

METHOD VALIDATION REPORT: [1]

The desorption efficiency, precision, bias and overall uncertainty data correspond to the data obtained in the validation of p-xylene. Since o-xylene, m-xylene, p-xylene and mixed xylenes have the same limit value, and assuming similar behaviour during collection in activated charcoal and subsequent desorption with carbon disulphide, the same validation data are assumed for the xylenes.

REFERENCES

[1] INSHT. *Determination of Aromatic Hydrocarbons (Benzene, Toluene, Ethylbenzene, p-Xylene, 1,2,4-Trimethylbenzene) in Air. Activated charcoal adsorption / Gas chromatography method.* MTA/MA – 030/A92.

OTHER METHODS

[2] OSHA. *Xylenes (o-, m-, p-Xylene), Ethylbenzene.* METHOD 1002 [*Activated charcoal tube / Gas chromatography (FID)*].

SULPHOTEP (TEDP) CAS No: 3689-24-5	SHEET No 52 October 2004
LV (8 h): 0.1 mg/m^3	

SUMMARY OF METHOD

The sample is collected by passing 240 l of air through a two-part sampler, composed of a quartz filter and a tube filled with XAD-2, using a personal sampling pump at a flow rate of 1 l/min. The sample is desorbed with a toluene / acetone solution and the resulting solution is analysed in a gas chromatograph equipped with a photometric detector (FPD).

SCOPE

The applicability of the method [1] to SULPHOTEP has not been confirmed.

The method [1] allows the simultaneous determination of other organophosphorous pesticides.

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: Quartz filter + adsorbent tube of XAD-2 (270 mg / 140 mg)

Sampling pump: personal type P

Recommended flow rate: 1 l/min

Recommended volume: 240 l

ANALYSIS

Preparation: desorption with 2 ml of toluene / acetone solution (9:1).

Analytical technique: gas chromatography with photometric detector (FPD) and DB-5, DB-1, DB-1701, DB-210 or similar capillary column.

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Desorption efficiency: no data available

Precision: no data available

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: medium

SULPHOTEP (TEDP) CAS No: 3689-24-5	SHEET No 52 October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method is not validated for SULPHOTEP (or TEDP), but it is validated for a large number of organophosphorous pesticides (19 in total) which gave a bias of less than 10% and overall precision of less than 7.1% for 240 l air samples at 1 l/min in the concentration range studied.
This validation was performed on spiked samples, over which 240 l of air was passed, with and without moisture.
The organophosphorous pesticide samples studied are stable for at least 10 days stored at room temperature and for 30 days stored at 0ºC.

ADAPTATION OF THE METHOD:

Although the validated method does not set a sampling volume for SULPHOTEP, 240 litres has been proposed because this is the volume recommended for most organophosphorous compounds [1] and is less than the maximum volume recommended for SULPHOTEP in another method that has been partially validated [2].

REFERENCES

[1] NIOSH. *Organophosphorous Pesticides*. Manual of Analytical Methods, 4th ed., Method 5600.

[2] OSHA. *Chemical Sampling Information. TEDP*. IMIS: 2327.

OTHER METHODS

HYDROGEN FLUORIDE

CAS No: 7664-39-3

SHEET No 53

October 2004

LV (8 h): 1.5 mg/m^3, 1.8 ppm

LV (short-term): 2.5 mg/m^3, 3 ppm

SUMMARY OF METHOD

The sample is collected by passing at least 120 l of air through a PTFE filter and a cellulose filter impregnated with a sodium carbonate and glycerine solution, using a personal sampling pump at a flow rate of 2 l/min. The PTFE filter is discarded and the impregnated filter is extracted with deionised water, a bicarbonate / carbonate buffer solution is added and the sample is analysed by ion chromatography with a conductivity detector.

SCOPE

The method is applicable to the determination of hydrogen fluoride, in the concentration range of 0.15 mg/m^3 to 3 mg/m^3, for 120 litre air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: breath sampler containing a 1 μm PTFE filter and a cellulose (paper) filter impregnated with a solution of 1M sodium carbonate and 5% (v/v) glycerine

Sampling pump: personal type P

Recommended flow rate: 2 l/min

Recommended volume: from 120 l

ANALYSIS

Preparation: the impregnated filter is extracted with 25 ml of deionised water, shaken for 30 minutes, and a bicarbonate / carbonate buffer solution is added.

Analytical technique: ion chromatography with conductivity detector and anion separation column.

TRANSPORT AND STORAGE

Samples are stable and do not require special storage conditions. Storage conditions are not stated in the method [1].

METHOD EVALUATION DATA

Recovery: 97.5% (CV = 7.0%)

Precision: 9.7%

Bias: 5%

Overall uncertainty: 24.4%

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: high

HYDROGEN FLUORIDE	SHEET No 53
CAS No: 7664-39-3	October 2004

OTHER INFORMATION OF INTEREST

This method is also applicable for comparison with the short-term limit value.
For sampling times of 15 minutes, and at the recommended flow rate (2 l/min), the amount collected will be 75 μg/sample, which lies within the application range for the method.
The PTFE filter traps particulate material (particulate fluorides) and the filter impregnated with sodium carbonate and glycerine captures mists of hydrofluoric acid, hydrogen fluoride and other gaseous fluorides.
The diameter of the collection medium filters must be appropriate for the breath sampler used (generally 25 or 37 mm).
Alternatively, when there is no exposure to hydrofluoric acid mists, samples can be collected with a three-part polystyrene cassette, using a filter of mixed cellulose esters to remove particulate material.

METHOD VALIDATION INFORMATION: [1]

The recovery and analytical precision shown in the sheet correspond to 36 filters spiked with fluoride at between 7.5 μg/filter and 300 μg/filter.

ADDITIONAL INFORMATION [1]:

The reference [1] states that fluoride analysis can also be performed by potentiometry with a specific electrode. Using the potentiometric analysis, the analytical precision obtained during validation with 36 impregnated filters spiked with fluoride at between 7.5 μg F^-/filter and 300 μg F^-/filter was 8.5%.
In this case, the filter is extracted with 5 ml of 2.5M hydrochloric acid for 30 minutes with occasional shaking. Twenty-five millilitres of 1M sodium citrate solution is added and the sample is allowed to stand for one hour with occasional shaking, then filtered and diluted to volume with deionised water.

REFERENCES

[1] HSE. *Hydrogen Fluoride and Fluorides in Air*. Methods for the Determination of Hazardous Substances. MDHS 35/2.

OTHER METHODS

[2] NIOSH. *Acids, Inorganic*. Manual of Analytical Methods, 4th ed., Method 7903.

[3] Cassinelli, M.E. *Laboratory Evaluation of Silica Gel Sorbent Tubes for Sampling Hydrogen Fluoride.* Am. Ind. Hyg. Assoc. J., 1986, 47(4): 219-224.

[4] INSHT. *Simultaneous determination of inorganic acid anions in air. Silica gel adsorption / Ion chromatography method*. Sampling and Analytical Methods. MTA/MA- 019/A90.

SILVER, metallic

CAS No: 7440-22-4

SHEET No 54-1

October 2004

LV (8 h): 0.1 mg/m^3

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a cellulose-ester membrane filter using a personal sampling pump at a flow rate of 1 l/min to 2 l/min. The sample is treated with hot concentrated nitric acid then hydrochloric acid, diluted with deionised water, and the resulting solution is analysed by aspiration into the flame of an atomic absorption spectrophotometer.

SCOPE

The method is applicable to the determination of silver, in the concentration range of 0.01 mg/m^3 to 0.2 mg/m^3, for air samples of 20 l to 100 l [1].

This method determines metallic silver and silver salts together [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: cellulose-ester membrane filter of 0.8 µm pore size and 37 mm diameter

Sampling pump: personal type P

Recommended flow rate: 1 l/min to 2 l/min

Recommended volume: 20 l to 100 l

ANALYSIS

Preparation: digest with 5 ml of hot conc. nitric acid until almost dry, add 1.5 ml of conc. hydrochloric acid, heat gently and dilute to 10 ml with deionised water.

Analytical technique: flame atomic absorption spectrophotometry.

TRANSPORT AND STORAGE

No specific precautions stated.

METHOD EVALUATION DATA

Precision: 8.3%

Bias: -2.2%

Overall uncertainty: 18.8%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: high

SILVER, metallic	SHEET No 54-1
CAS No: 7440-22-4	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION [1]:

The precision and bias shown in the sheet correspond to 270 filters spiked with silver at between 1 µg and 4 µg per filter.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **100 l** must be sampled for concentrations of 0.1 LV (0.01 mg/m^3) to 0.5 LV (0.05 mg/m^3) and at least **20 l** for concentrations of 0.5 LV (0.05 mg/m^3) to 2 LV (0.2 mg/m^3) at a flow rate of 1 l/min to 2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] OSHA. *Metal & Metalloid Particulates in Workplace Atmospheres (Atomic Absorption*). Sampling & Analytical Methods, Method No ID-121.

OTHER METHODS

[2] INSHT. *Determination of Metals and Their Ionic Compounds in Air. Membrane filter / Atomic absorption spectrophotometry method*. Sampling and Analytical Methods. MTA/MA- 025/A92.

[3] OSHA. *ICP Analysis of Metal / Metalloid Particulates from Solder Operations*. Sampling & Analytical Methods, Method No ID-206.

[4] OSHA. *ICP Backup Data Report for OSHA Method No ID-206 for Soldering-Brazing Matrices (ARL 3560).*

[5] NIOSH. *Elements by ICP*. Manual of Analytical Methods, 4th ed., Method 7300.

SILVER, metallic

CAS No: 7440-22-4

SHEET No 54-2

October 2004

LV (8 h): 0.1 mg/m^3

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a cellulose-ester membrane filter using a personal sampling pump at a flow rate of 2 l/min. The sample is treated with a mixture of hot concentrated hydrochloric and nitric acids, diluted with deionised water, and the resulting solution is analysed by inductively coupled plasma - atomic emission spectroscopy (ICP-AES).

SCOPE

The method is applicable to the determination of silver, in the concentration range of 0.01 mg/m^3 to 0.2 mg/m^3, for air samples of 50 l to 220 l [1].

This method determines metallic silver and silver salts together.

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: cellulose-ester membrane filter of 0.8 μm pore size and 37 mm diameter

Sampling pump: personal type P

Recommended flow rate: 2 l/min

Recommended volume: 50 l to 220 l

ANALYSIS

Preparation: the filter is treated with 8 ml of hot conc. hydrochloric acid and 2 ml of hot conc. nitric acid. The volume is reduced to 0.5 ml, 3 ml of conc. hydrochloric acid is added and the sample is diluted to 10 ml with deionised water.

Analytical technique: inductively coupled plasma - atomic emission spectroscopy (ICP-AES).

TRANSPORT AND STORAGE

No specific precautions stated.

METHOD EVALUATION DATA

Precision: 6.6% [1]

Bias: 3.6% [1]

Overall uncertainty: 16.9% [1]

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: high

SILVER, metallic	SHEET No 54-2
CAS No: 7440-22-4	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION [1]:

The precision and bias shown in the sheet correspond to 18 filters spiked with silver at between 2.2 µg/filter and 10.1 µg/filter.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **220 l** must be sampled for concentrations of 0.1 LV (0.01 mg/m^3) to 0.5 LV (0.05 mg/m^3) and at least **50 l** for concentrations of 0.5 LV (0.05 mg/m^3) to 2 LV (0.2 mg/m^3) at a flow rate of 1 l/min to 2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] OSHA. *ICP Backup Data Report for OSHA Method No ID-206 for Soldering-Brazing Matrices (ARL 3560).*

[2] OSHA. *ICP Analysis of Metal / Metalloid Particulates from Solder Operations*. Sampling & Analytical Methods, Method No ID-206.

OTHER METHODS

[3] NIOSH. *Elements by ICP*. Manual of Analytical Methods, 4th ed., Method 7300.

[4] INSHT. *Determination of Metals and Their Ionic Compounds in Air. Membrane filter / Atomic absorption spectrophotometry method*. Sampling and Analytical Methods. MTA/MA- 025/A92.

[5] OSHA. *Metal & Metalloid Particulates in Workplace Atmospheres (Atomic Absorption*). Method No ID-121.

HYDROGEN CHLORIDE

CAS No: 7647-01-0

SHEET No 55

October 2004

LV (8 h): 8 mg/m^3, 5 ppm

LV (short-term): 15 mg/m^3, 10 ppm

SUMMARY OF METHOD

The sample is collected by passing 15 l of air through a tube filled with 400 / 200 mg of silica gel preceded by a plug of silanised glass wool, using a personal sampling pump at a flow rate of 0.2 l/min. The sample can be stored at room temperature for 21 days. The sample is desorbed with hot bicarbonate / carbonate buffer solution and the resulting solution is analysed in an ion chromatograph equipped with a conductivity detector.

SCOPE

The method is applicable to the determination of hydrogen chloride, in the concentration range of 0.8 mg/m^3 to 16 mg/m^3, for 15 l air samples [1].

This method allows the simultaneous determination of anions of other inorganic acids, such as hydrogen fluoride, hydrogen bromide, nitric acid, orthophosphoric acid and sulphuric acid [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: tube of silica gel (400 / 200 mg) of 20 / 40 mesh, preceded by a silanised glass-wool plug (or a glass-fibre filter of 6 mm diameter and 1 mm thick)

Sampling pump: personal type G

Recommended flow rate: 0.2 l/min

Recommended volume: 15 l

ANALYSIS

Preparation: the first section of silica gel and the glass-wool plug are desorbed together, with 10 ml of bicarbonate / carbonate buffer solution (1.7 mM / 1.8 mM) for 10 minutes in a boiling water bath.

Analytical technique: ion chromatography with conductivity detector and anion separation column.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Precision: 5.9%

Bias: not available

Overall uncertainty: not available

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: high

HYDROGEN CHLORIDE	SHEET No 55
CAS No: 7647-01-0	October 2004

OTHER INFORMATION OF INTEREST

This method is also applicable for comparison with the short-term limit value.
For sampling times of 15 minutes, and at the recommended flow rate (0.2 l/min), the amount collected will be 4.5 μg/sample, which lies within the application range for the method.
Hydrogen chloride salt particles cause interference.

METHOD VALIDATION INFORMATION [1]:

The method [1] is validated for the concentration range of 0.14 mg/m^3 to 14 mg/m^3. This range includes the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The precision shown in the sheet corresponds to the whole set of samples collected in the concentration range of 0.14 mg/m^3 to 14 mg/m^3 of hydrogen chloride.
Hydrogen chloride salt particles, if present, will be trapped in the silanised glass-wool plug (or glass-fibre filter).

ADDITIONAL INFORMATION:

NIOSH method 7903 [1] does not specify the sampling volume for hydrogen chloride, but says it is a revised version of P&CAM 339 [4] which recommends a collection volume of 15 litres. This is the recommended volume shown in the sheet.

REFERENCES

[1] NIOSH. *Acids, Inorganic*. Manual of Analytical Methods, 4th ed., Method 7903.

OTHER METHODS

[2] INSHT. *Simultaneous Determination of Inorganic Acid Anions in Air. Silica gel adsorption / Ion chromatography method*. Sampling and Analytical Methods. MTA/MA- 019/A90.

[3] DFG. *Volatile Inorganic Acids (HCl, HBr, HNO_3)*. Analyses of Hazardous Substances in Air. Vol. 6, p. 211.

[4] NIOSH. *Inorganic Acids*. Manual of Analytical Methods, 2nd ed., Vol. 7, P&CAM 339.

ORTHOPHOSPHORIC ACID **CAS No: 7664-38-2**	**SHEET No 56** **October 2004**
LV (8 h): 1 mg/m^3	**LV (short-term):** 2 mg/m^3

SUMMARY OF METHOD

The sample is collected by passing 420 l of air through a quartz filter, using a personal sampling pump at a flow rate of 3.5 l/min. Samples can be stored for at least one week at room temperature and for 28 days in a refrigerator. The sample is desorbed with a bicarbonate / carbonate buffer solution and the resulting solution is filtered and analysed in an ion chromatograph equipped with a conductivity detector.

SCOPE

The method is applicable to the determination of orthophosphoric acid, in the concentration range of 0.1 mg/m^3 to 2 mg/m^3, for 420 l air samples [1].

This method allows the simultaneous determination of sulphuric acid [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: filter holder or cassette with a quartz filter of 37 mm diameter

Sampling pump: personal type P

Recommended flow rate: 3.5 l/min

Recommended volume: 420 l

ANALYSIS

Preparation: desorb the filter with 4 ml of bicarbonate / carbonate solution (0.3 mM / 2.7 mM), shake carefully, place into an ultrasonic bath for 15 minutes and filter the solution.

Analytical technique: ion chromatography with conductivity detector.

TRANSPORT AND STORAGE

Samples prepared by deposition do not display any loss when stored for 4 weeks, at room temperature for the first week and in the refrigerator for the remaining period.

METHOD EVALUATION DATA

Precision: 3.2%

Bias: -3%

Overall uncertainty: 9.4%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: high

ORTHOPHOSPHORIC ACID	SHEET No 56
CAS No: 7664-38-2	October 2004

OTHER INFORMATION OF INTEREST

This method can also be used for comparison with the short-term limit value.
For sampling times of 15 minutes, and at the recommended flow rate (3.5 l/min), the amount collected will be 105 μg/sample, which lies within the application range for the method.
Salt particles of orthophosphoric acid cause interference.

METHOD VALIDATION INFORMATION [1]:

The method [1] is validated for the concentration range of 0.01 mg/m^3 to 2 mg/m^3. This range includes the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.
The method has been validated, with samples prepared by deposition, for the determination of orthophosphoric acid in the concentration range of 0.01 mg/m^3 to 2 mg/m^3, for 420 litre air samples, equivalent to 4.2 μg/sample and 840 μg/sample.

REFERENCES

[1] DFG. *Inorganic Acid Mists (H_2SO_4, H_3PO_4)*. Analyses of Hazardous Substances in Air. Vol. 6, p. 67.

OTHER METHODS

[2] NIOSH. *Acids, Inorganic.* Manual of Analytical Methods, 4th ed., Method 7903.

[3] INSHT. *Simultaneous Determination of Inorganic Acid Anions in Air. Silica gel adsorption / Ion chromatography method*. Sampling and Analytical Methods. MTA/MA- 019/A90.

[4] OSHA. *Acid Mist in Workplace Atmospheres*. Method No ID-165SG.

AMMONIA, anhydrous CAS No: 7664-41-7	SHEET No 57 October 2004
LV (8 h): 14 mg/m^3, 20 ppm	**LV (short-term):** 36 mg/m^3, 50 ppm

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a tube filled with 500 / 250 mg of carbon beads treated with sulphuric acid, preceded by a cellulose-ester membrane filter of 37 mm diameter and 0.8 µm pore size, using a personal sampling pump at a flow rate of 0.5 l/min. The sample can be stored for at least one month at room temperature. The sample is desorbed with deionised water and the resulting solution is analysed in an ion chromatograph equipped with a conductivity detector.

SCOPE

The method is applicable to the determination of ammonia, in the concentration range of 2.8 mg/m^3 (0.2 LV) to 28 mg/m^3 (2 LV), for samples of 60 litres to 160 litres [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: mixed cellulose ester filter of 37 mm and 0.8 µm + tube of carbon beads (500 / 250 mg) of 20 / 30 mesh impregnated with sulphuric acid

Sampling pump: multi-purpose personal

Recommended flow rate: 0.5 l/min

Recommended volume: 60 l to 160 l

ANALYSIS

Preparation: each section of the tube is desorbed with 10 ml of deionised water, shaken vigorously for 30 seconds and left to stand for at least 1 hour.

Analytical technique: ion chromatography with conductivity detector and cation separation column.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 29 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 99.7% (CV = 3.1%) [2]

Precision: 7.7% [2]

Bias: 3.4% [2]

Overall uncertainty: 18.8% [2]

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: high

AMMONIA, anhydrous	SHEET No 57
CAS No: 7664-41-7	October 2004

OTHER INFORMATION OF INTEREST

The applicability of the method for making measurements for comparison with the short-term limit value has not been confirmed.

For sampling times of 15 minutes, and at the recommended flow rate (0.5 l/min), the amount collected will be 270 μg/sample, which is outside the application range for the method.

The filter is used to prevent interference from particles or ammonium salts [1].

METHOD VALIDATION INFORMATION [1] [2]:

The method [1] is validated for the concentration range of 21.8 mg/m^3 to 72.2 mg/m^3. This range does not coincide with the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 21 l air samples, collected at 0.1 l/min in generated atmospheres, with 50% mean humidity, in the concentration range of 21.8 mg/m^3 to 72.2 mg/m^3 of ammonia, equivalent to 460 μg/sample and 1520 μg/sample [2].

The desorption efficiency corresponds to the average of 20 samples in the range of 350 μg/sample to 1640 μg/sample [2].

When samples of 183 mg/m^3 were collected, generated with 50% humidity and at 25ºC, no breakthrough was observed after sampling for 335 minutes at a flow rate of 0.1 l/min (6000 μg ammonia/sample) [1] [2].

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **160 l** must be sampled for concentrations of 0.2 LV (2.8 mg/m^3) to 0.5 LV (7 mg/m^3) and at least **60 l** for concentrations of 0.5 LV (7 mg/m^3) to 2 LV (28 mg/m^3) at a flow rate of 0.5 l/min, i.e. the sampling conditions shown in the sheet. This flow rate of 0.5 l/min is the rate recommended for short-term measurements [1], so can be regarded as appropriate for collecting the necessary sample volume.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] OSHA. *Ammonia in Workplace Atmospheres. Solid sorbent*. Method No ID-188.

[2] OSHA. *Ammonia Backup Data Report. Method No ID-188*.

OTHER METHODS

[3] NIOSH. *Ammonia by IC*. Manual of Analytical Methods, 4th ed., Method 6016. *Collection by adsorbent tube of silica gel treated with sulphuric acid with ion chromatographic analysis.*

[4] NIOSH. *Ammonia.* Manual of Analytical Methods, 2nd ed., Vol. 5, Method S347. *Collection by tube of silica gel treated with sulphuric acid and potentiometric analysis of ammonium ion.*

[5] DFG. *Ammonia*. Analyses of Hazardous Substances in Air. Vol. 2, pp. 31-41. *Collection via sulphuric acid solution and colorimetric analysis of ammonium ion.*

[6] INRS. *Ammonia and Ammonium Salts*. Sheet 013. *Collection by quartz filter impregnated with sulphuric acid and glycerine and ion chromatographic analysis.*

FLUORINE CAS No: 7782-41-4	SHEET No 58 October 2004
LV (8 h): 1.58 mg/m^3, 1 ppm	**LV (short-term):** 3.16 mg/m^3, 2 ppm

SUMMARY OF METHOD

The sample is collected by passing up to 480 l of air through a fritted bubbler containing a dilute sodium hydroxide solution, using a personal sampling pump at a maximum flow rate of 1 l/min. The fluoride ion content of the resulting solution is analysed potentiometrically using a specific electrode.

SCOPE

Not determined.

This method allows fluorine, hydrogen fluoride and other gaseous fluorides to be collected and determined together.

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: fritted bubbler containing 15 ml of 0.1N sodium hydroxide [1]

Sampling pump: personal type P

Recommended flow rate: 1 l/min at most [1]

Recommended volume: 480 l at most [1]

ANALYSIS

Preparation: the sample solution from each bubbler is diluted to 25 ml with 0.1N NaOH. A volume of the resulting solution is removed and mixed with an equal volume of TISAB (total ionic strength adjustment buffer) [2].

Analytical technique: potentiometric analysis with a specific fluoride ion electrode [2].

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Collection efficiency: no data available

Precision: no data available

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: low

FLUORINE	SHEET No 58
CAS No: 7782-41-4	October 2004

OTHER INFORMATION OF INTEREST

Fluorine is converted to fluoride ion when bubbled through a sodium hydroxide solution and its equivalent concentration can be determined using a method for hydrogen fluoride or fluorides.

METHOD VALIDATION INFORMATION [1] [2]:
The sampling and analytical method described in the sheet has not been validated as a whole.

PROPOSED METHOD:
The method described in the sheet is actually a proposed method, because no validated method for fluorine determination is currently available.
The proposal consists of fluorine **collection** in a dilute sodium hydroxide solution, as described in reference **[1],** and subsequent **potentiometric determination** of fluoride ion using a specific electrode, as described in reference **[2].**
Reference [1] only gives maximum sampling figures: a flow rate of 1 l/min and a volume of 480 litres.

NOTE
The OSHA ID-110 method [3] described in reference [1], for the analytical determination of **fluoride ion** content, uses a filter to collect the sample, whereas the validated NIOSH S-176 method [2] is based on collection in a 0.1N NaOH solution and subsequent potentiometric determination of fluoride ion using a specific electrode.

REFERENCES

[1] OSHA. *Chemical Sampling Information.* IMIS: 1270, USA.

[2] NIOSH. *Hydrogen Fluoride*. Manual of Analytical Methods, 2nd ed., Vol. 3, Method S-176.

OTHER METHODS

[3] OSHA. *Fluoride (F^- and HF) in Workplace Atmospheres*. Method No ID-110.

[4] OTEY M.G., PULLEY H. *Determination of Gaseous Fluorine in Air*. Am. Ind. Hyg. Assoc. J. 1973; 34: 418-20.

[5] LYON J.S. *Observations on Personnel Working with Fluorine at a Gaseous Diffusion Plant*. J. of Occup. Med., 1962, Vol. 4 (49): 199-201.

HYDROGEN SELENIDE CAS No: 7783-07-5	SHEET No 59 October 2004
LV (8 h): 0.07 mg/m^3, 0.02 ppm	**LV (short-term):** 0.17 mg/m^3, 0.05 ppm

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a fritted bubbler containing 10 ml of deionised water at a maximum flow rate of 1 l/min. The resulting solution is analysed by electrothermal atomic absorption spectrophotometry with a graphite chamber (EAAS).

SCOPE

The application range has not been defined.

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: fritted bubbler containing 10 ml of deionised water

Sampling pump: personal type P

Recommended flow rate: 1 l/min at most

Recommended volume: 240 l to 480 l

ANALYSIS

Preparation: the resulting sample solution is made up to volume.

Analytical technique: electrothermal atomic absorption spectrophotometry with graphite chamber (EAAS).

TRANSPORT AND STORAGE

Not studied.

METHOD EVALUATION DATA

Precision: no data available

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: high

HYDROGEN SELENIDE	SHEET No 59
CAS No: 7783-07-5	October 2004

OTHER INFORMATION OF INTEREST

The data shown in the sheet are the details given in the bibliographic reference [1] which proposes analysing the selenium corresponding to the collected hydrogen selenide using the OSHA ID-105 method, validated for inorganic arsenic by graphite absorption with a graphite chamber [2].

ADDITIONAL INFORMATION:

OSHA also has a partially validated method for sampling and analysing selenium in air, based on the determination of selenium by atomic absorption with a graphite chamber [3].

REFERENCES

[1] OSHA. *Hydrogen Selenide (as Se)*. IMIS 1474.

[2] OSHA. *Inorganic Arsenic in Workplace Atmospheres*. Method No ID-105.

OTHER METHODS

[3] OSHA. *Selenium*. Method No ID-1335G.

[4] HETLAND, S. *et al.* *Species analysis of inorganic compounds in workroom air by Atomic Espectroscopy*. Analytical Sciences, Supplement 1991, Vol. 7, 1029-1032.

[5] Criteria document for hydrogen selenide. Occupational exposure limits. Health and Safety. Report EUR 14239 EN (1992).

[6] Arbeidsmilj Instituttet (1990). Personal communication. National Institute of Occupational Health, Glydas vei 8, PB 8149 Dep N-0033.

HYDROGEN BROMIDE

CAS No: 10035-10-6

SHEET No 60

October 2004

LV (short-term): 6.7 mg/m^3, 2 ppm

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a tube filled with 400 / 200 mg of silica gel preceded by a plug of silanised glass wool, using a personal sampling pump at a flow rate of 0.2 l/min to 0.5 l/min. The sample can be stored at room temperature for 21 days. The sample is desorbed with hot sodium carbonate / bicarbonate buffer solution and the resulting solution is analysed in an ion chromatograph equipped with a conductivity detector.

SCOPE

This method has not been developed for comparison with the short-term limit value (see modifications to the method).

The method is applicable to the determination of hydrogen bromide, in the concentration range of 2 mg/m^3 to 20 mg/m^3, for 50 l air samples [1].

This method allows the simultaneous determination of anions of other inorganic acids, such as hydrogen fluoride, hydrogen chloride, nitric acid, orthophosphoric acid and sulphuric acid.

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: tube of silica gel (400 / 200 mg) of 20 / 40 mesh, preceded by a silanised glass-wool plug (or a glass-fibre filter of 6 mm diameter and 1 mm thick)

Sampling pump: personal type P

Recommended flow rate: 0.2 l/min to 0.5 l/min [1]

Recommended volume: ≥ 15 l

ANALYSIS

Preparation: each section of tube is desorbed with 10 ml of bicarbonate / carbonate solution (1.7 mM / 1.8 mM) for 10 minutes in a boiling water bath.

Analytical technique: ion chromatography with conductivity detector and anion separation column.

TRANSPORT AND STORAGE

Samples do not display any loss when stored at room temperature after completion of sampling and analysed within 21 days of collection.

METHOD EVALUATION DATA

Precision: no data available

Bias: no data available

Overall uncertainty: no data available

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: high

HYDROGEN BROMIDE	SHEET No 60
CAS No: 10035-10-6	October 2004

OTHER INFORMATION OF INTEREST

Hydrogen bromide salt particles cause interference.

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the determination of hydrogen bromide, in the concentration range of 2 mg/m^3 to 20 mg/m^3, for 50 litre air samples, equivalent to 100 μg/sample and 1000 μg/sample.
Hydrogen bromide salt particles, if present, will be trapped in the silanised glass-wool plug (or in the glass-fibre filter).

NOTES

The applicability of the method for hydrogen bromide measurements for comparison with the short-term limit value has not been confirmed.
For sampling times of 15 minutes, and at the maximum recommended flow rate (0.5 l/min), the amount collected will be 50 μg/sample, which is outside the application range for the method. To increase the amount collected to 100 μg/sample (lower limit of the studied range), it would be necessary to sample at least 15 l at 1 l/min.
Since this is a gas, this modification would need to be checked by calculating the breakthrough volume at that flow rate, because humidity and flow rate influence the collection capacity of the sampler.

REFERENCES

[1] NIOSH. *Acids, Inorganic*. Manual of Analytical Methods, 4th ed., Method 7903.

OTHER METHODS

[2] DFG. *Volatile Inorganic Acids (HCl, HBr, HNO_3)*. Analyses of Hazardous Substances in Air, Vol. 6 p. 211. [*Collection by tube of silica gel and ion chromatographic analysis*].

[3] INSHT. *Simultaneous Determination of Inorganic Acid Anions in Air. Silica gel adsorption / Ion chromatography method*. Sampling and Analytical Methods. MTA/MA- 019/A90. [*Collection by tube of silica gel and ion chromatographic analysis*].

[4] NIOSH. *Hydrogen Bromide*. Manual of Analytical Methods, 2nd ed., Vol. 3, Method S-175. [*Collection by impinger and potentiometric analysis with specific electrode*].

SODIUM AZIDE	SHEET No 61
CAS No: 26628-22-8	October 2004

LV (8 h): 0.1 mg/m^3	LV (short-term): 0.3 mg/m^3

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a tube filled with 150 / 75 mg of silica gel impregnated with a base, preceded by a PVC pre-filter, using a personal sampling pump at a flow rate of 1 l/min. The sample should be sent to the laboratory as soon as possible and stored in a refrigerator. The sample is desorbed with a sodium carbonate / bicarbonate solution and the resulting solution is analysed in an ion chromatograph equipped with a UV detector.

SCOPE

The method is applicable to the determination of sodium azide, in the concentration range of 0.01 mg/m^3 to 0.2 mg/m^3, for air samples of 15 l to 75 l [1].

This method determines particles of sodium azide (NaN_3) and vapours of hydrazoic acid (HN_3), and its use can be extended to other azide compounds.

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: PVC filter of 37 mm diameter and 5 μm pore size + adsorbent tube of silica gel (150 / 75 mg) impregnated with sodium hydroxide

Sampling pump: personal type P

Recommended flow rate: 1 l/min

Recommended volume: 15 l to 75 l

ANALYSIS

Preparation: the filter is desorbed with 5 ml of carbonate / bicarbonate solution (0.9 mM / 0.9 mM). The first section of tube and the glass-wool plug are desorbed together with 3 ml of desorbent solution. Allow to stand for at least 60 min., with occasional shaking.

Analytical technique: ion chromatography with variable UV detector at 210 nm.

TRANSPORT AND STORAGE

Samples do not display significant loss if stored at room temperature after completion of sampling and analysed within 10 days. However, it is advisable to send them to the laboratory as soon as possible and store them in a refrigerator until analysed. Refrigerated samples do not display significant loss after 30 days.

METHOD EVALUATION DATA

Desorption efficiency: 100.1% (CV = 2.3%)

Precision: 5.3%

Bias: -4.5%

Overall uncertainty: 15.1%

OTHER CHARACTERISTICS

Degree of difficulty: complex application

Financial cost: high

SODIUM AZIDE	SHEET No 61
CAS No: 26628-22-8	October 2004

OTHER INFORMATION OF INTEREST

The method is applicable for comparison with the short-term limit value.
For sampling times of 15 minutes, and at the recommended flow rate (1 l/min), the amount collected will be 4.5 μg/sample, which lies within the application range for the method.
Hydrazoic acid (HN_3) vapour coexists with sodium azide (NaN_3) in the workplace when azide is collected in the presence of moisture. Sodium azide particles are trapped in the PVC filter or glass-wool plug of the sampling tube. Hydrazoic acid is collected and converted to sodium azide in the adsorbent tube of silica gel impregnated with sodium hydroxide.
The PVC pre-filter can be replaced by a type A glass-fibre filter.

METHOD VALIDATION INFORMATION: [1]

The method has been validated for 5 litre air samples in the concentration range of 0.057 ppm to 0.263 ppm as hydrazoic acid (HN_3), which is equivalent to 0.15 mg/m^3 and 0.71 mg/m^3 as sodium azide (0.75-3.55 μg/sample).
When samples generated with a hydrazoic acid concentration of 0.9 ppm (equivalent to 2.43 mg/m^3 as sodium azide) were collected, no breakthrough was observed after sampling for 30 minutes at a flow rate of 1 l/min (73 μg/sample).

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **75 l** must be sampled for concentrations of 0.1 LV (0.01 mg/m^3) to 0.5 LV (0.05 mg/m^3) and at least **15 l** for concentrations of 0.5 LV (0.05 mg/m^3) to 2 LV (0.2 mg/m^3) at a flow rate of 1 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

REFERENCES

[1] OSHA. *Sodium Azide and Hydrazoic in Workplace Atmospheres*. Method No ID-211.

OTHER METHODS

1-METHYL-2-METHOXYETHOXY-PROPANOL **CAS No: 34590-94-8**	**SHEET No 62** **October 2004**
LV (8 h): 308 mg/m^3, 50 ppm	

SUMMARY OF METHOD

The sample is collected by passing 10 l of air through a tube filled with 100 / 50 mg of activated charcoal using a personal sampling pump at a flow rate of 0.1 l/min to 0.2 l/min. The sample can be stored at room temperature for 15 days. The 2-methoxymethylethoxy-propanol is desorbed with 1 ml of dichloromethane containing 5% methanol and the resulting solution is analysed in a gas chromatograph equipped with a flame ionisation detector.

SCOPE

The method is applicable to the determination of 2-methoxymethylethoxy-propanol vapours in air, in the concentration range of 30 mg/m^3 to 600 mg/m^3, for 10 l air samples [1].

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: standard tube of activated charcoal (100 mg / 50 mg)

Sampling pump: personal type G

Recommended flow rate: 0.1 l/min to 0.2 l/min

Recommended volume: 10 l

ANALYSIS

Preparation: desorption with 1 ml of dichloromethane containing 5% (v/v) methanol.

Analytical technique: gas chromatography with FFAP capillary column, or any other capable of separating the analytes of interest, and flame ionisation detector.

TRANSPORT AND STORAGE

Samples do not display significant loss when stored at room temperature after completion of sampling and analysed within 15 days of collection.

METHOD EVALUATION DATA

Desorption efficiency: 98.6% (CV = 1.1%)

Precision: 0.1%

Bias: 0.2%

Overall uncertainty: 0.4%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

1-METHYL-2-METHOXYETHOXY-PROPANOL	SHEET No 62
CAS No: 34590-94-8	October 2004

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The method [1] is validated for the concentration of 606 mg/m^3 (2 LV). This value coincides with the upper limit of the concentration range of 0.1 LV to 2 LV in relation to the current 8-hour limit value.

The precision and bias shown in the sheet correspond to 10 l air samples, collected in atmospheres generated with moisture, at a concentration of 606 mg/m^3, equivalent to 6000 µg/sample.

The desorption efficiency corresponds to the average of 30 samples in the range of 300 µg/sample to 12000 µg/sample.

REFERENCES

[1] OSHA. *Dipropylene Glycol Methyl Ether.* METHOD 101.

OTHER METHODS

FLUORIDES, INORGANIC **CAS No:**	**SHEET No 63** **October 2004**
LV (8 h): 2.5 mg/m^3	

SUMMARY OF METHOD

The sample is collected by passing at least 150 l of air through a cellulose-ester filter and a cellulose filter that has been impregnated with sodium carbonate and glycerine solution, using a personal sampling pump at a flow rate of 2 l/min. The filters are extracted together, with a hydrochloric acid solution and a sodium citrate solution. The resulting solution is analysed in a potentiometer equipped with a specific fluoride ion electrode.

SCOPE

The method is applicable to the determination of total fluorides, in the concentration range of 0.25 mg/m^3 to 5 mg/m^3, for 150 litre air samples [1].

This method allows total fluorides (as F^-), particulate and gaseous, to be determined together or differentiated if the two filters are analysed separately.

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: breath sampler containing a 0.8 µm mixed cellulose ester filter and a cellulose (paper) filter impregnated with a solution of 1M sodium carbonate and 5% (v/v) glycerine
Sampling pump: personal type P
Recommended flow rate: 2 l/min
Recommended volume: at least 150 l

ANALYSIS

Preparation: the filters are extracted together with 2.5M hydrochloric acid for 30 min. with occasional shaking. Add 1M sodium citrate solution and leave to stand for 1 hour with occasional shaking. Filter and dilute to volume with deionised water.

Analytical technique: potentiometry with a specific fluoride ion electrode.

TRANSPORT AND STORAGE

Samples are stable and do not require special storage conditions.

METHOD EVALUATION DATA

Recovery: 100.4% (CV = 3.3%) particulate F^- and 97.5% (CV = 7.0%) gaseous F^-

Precision: 5.3% (particulate F^-) and 8.5% (gaseous F^-)

Bias: 5%

Overall uncertainty: 15.6% (particulate F^-) and 22% (gaseous F^-)

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: low

FLUORIDES, INORGANIC	SHEET No 63
CAS No:	October 2004

OTHER INFORMATION OF INTEREST

The diameter of the collection medium filters must be appropriate for the breath sampler used (generally 25 or 37 mm).
The cellulose-ester membrane filter traps particulate fluorides and the cellulose filter impregnated with sodium carbonate and glycerine traps mists of hydrofluoric acid, hydrogen fluoride and other gaseous fluorides.
Alternatively, when there is no exposure to gaseous fluorides and/or hydrofluoric acid mists, the impregnated filter can be omitted and the mixed cellulose-ester filter used alone as a collection medium for particulate fluorides.

METHOD VALIDATION INFORMATION: [1]

The recovery and analytical precision values shown in the sheet correspond to 36 impregnated cellulose filters spiked with fluorides at between 7.5 μg/filter and 300 μg/filter (gaseous fluorides) and 96 cellulose-ester membrane filters spiked with fluorides at between 36 μg/filter and 4800 μg/filter (particulate fluorides).

ADAPTATION OF THE METHOD:

In order to be able to use the recovery and precision values from the validated method, in the case of particulate fluorides, and relate them to the current 8-hour limit value, a recommended sampling volume must be set. For the amount collected to correspond, for particulate fluoride air concentrations of 0.1 LV to 2 LV, at least **150 l** must be sampled**,** at a flow rate of 2 l/min, i.e. the sampling conditions shown in the sheet.

ADDITIONAL INFORMATION:

Some particulate fluorides can only be solubilised by treating the sample more vigorously, for example by alkaline melt. An alternative method should be used in such cases [2].

REFERENCES

[1] HSE. *Hydrogen Fluoride and Fluorides in Air.* MDHS 35/2.

OTHER METHODS

[2] OSHA. *Fluoride (F^- and HF) in Workplace Atmospheres*. Method ID-110.

Treatment by alkaline melt in a crucible. The residue is dissolved in water and neutralised with hydrochloric acid. Tris-tartrate (T-T) buffer solution is added, followed by potentiometric analysis with a specific fluoride ion electrode. The method is validated for an application range of 350 μg to 770 μg of F^-/sample.

ANNEX 6

ANALYTICAL METHOD SHEETS FOR LEAD AND ITS IONIC COMPOUNDS IN AIR AND BLOOD

LEAD in blood

CAS No: 110-85-0

SHEET No 64

October 2004

BLV: 75 µg of Pb/100 ml of blood

SUMMARY OF METHOD

Blood samples are collected in polyethylene tubes containing EDTA-K_2 (dipotassium salt of ethylenediamine tetraacetic acid) as an anticoagulant.

The blood is diluted with a surfactant to facilitate haemolysis. The lead present is quantified by atomic absorption spectrophotometry at 283.3 nm, using a graphite chamber with L'vov platform and matrix modification.

SCOPE

This method allows the determination of lead in blood in the concentration range of 5 to 100 µg of Pb/100 ml of blood (0.24 to 4.82 µmol/litre) and can be used for monitoring the working population potentially exposed to metallic lead and its ionic compounds.

TECHNICAL CHARACTERISTICS

SAMPLING

The sample of venous blood taken in a polyethylene or polystyrene syringe is collected into 5 ml polyethylene tubes containing EDTA-K_2 as an anticoagulant and mixed carefully.

ANALYSIS

Preparation: 50 µl of blood + 600 µl of matrix modifier (ammonium (V) dihydrogen phosphate).

Analytical technique: atomic absorption spectrophotometry at 283.3 nm, using a graphite chamber with L'vov platform.

TRANSPORT AND STORAGE

Samples do not display any loss when stored in a refrigerator and analysed within 15 days of collection.

METHOD EVALUATION DATA

Precision: 2.5%

Bias: not significant

Overall uncertainty: 5%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: medium

LEAD in blood **CAS No: 110-85-0**	**SHEET No 64** **October 2004**

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION:

This method has been validated using BCR certified reference materials (CRM Nos 194, 195 and 196). It has also been the subject of an inter-laboratory comparison test conducted in accordance with ISO 5725 which provided method repeatability and reproducibility.

The limit of detection for lead in blood, calculated using a real sample of concentration close to the blank and in accordance with the IUPAC definition, is 1.5 µg Pb/100 ml of blood.

REFERENCES

[1] INSHT. *Determination of Lead in Blood. Graphite chamber / atomic absorption spectrometry method.* MTA/MB-011/R92.

OTHER METHODS

LEAD, inorganic and its compounds

CAS No: 7439-92-1

SHEET No 65

October 2004

LV (8 h): 0.15 mg/m^3

SUMMARY OF METHOD

The sample is collected by passing a volume of air through a cellulose-ester membrane filter using a personal sampling pump at a flow rate of 2 l/min. The sample is treated with a mixture of hot concentrated hydrochloric and nitric acids and diluted with deionised water. The resulting solution is analysed by inductively coupled plasma - atomic emission spectroscopy (ICP-AES).

SCOPE

The method is applicable to the determination of lead, in the concentration range of 0.015 mg/m^3 to 0.3 mg/m^3, for air samples of 160 to 700 litres.

This method allows the simultaneous determination of other metallic elements or compounds.

TECHNICAL CHARACTERISTICS

SAMPLING

Collection medium: cellulose-ester membrane filter of 0.8 µm pore size and 37 mm diameter

Sampling pump: personal type P

Recommended flow rate: 2 l/min

Recommended volume: 160 l to 700 l

ANALYSIS

Preparation: the filter is treated with 8 ml of hot conc. hydrochloric acid and 2 ml of hot conc. nitric acid. The volume is reduced to 0.5 ml, 3 ml of conc. hydrochloric acid is added and the sample is diluted to 10 ml with deionised water.

Analytical technique: inductively coupled plasma - atomic emission spectroscopy (ICP-AES).

TRANSPORT AND STORAGE

No specific precautions are specified.

METHOD EVALUATION DATA

Precision: 6.0%

Bias: -3.8%

Overall uncertainty: 15.8%

OTHER CHARACTERISTICS

Degree of difficulty: simple application

Financial cost: high

OTHER INFORMATION OF INTEREST

METHOD VALIDATION INFORMATION: [1]

The precision and bias shown in the sheet correspond to 18 filters spiked with lead at between 11 µg and 48 µg of lead per sample.

ADAPTATION OF THE METHOD:

In order to use the method [1], taking advantage of the validation information, it must be adapted to the current scope of interest defined in relation to the LV.

The best way is to adjust the sampling volume so that the amount of sample collected lies within the concentration range for which the method was validated. To do this, at least **700 l** must be sampled for concentrations of 0.1 LV (0.016 mg/m^3) to 0.5 LV (0.069 mg/m^3) and at least **160 l** for concentrations of 0.5 LV (0.069 mg/m^3) to 2 LV (0.3 mg/m^3) at a flow rate of 2 l/min, i.e. the sampling conditions shown in the sheet.

This approximation allows the precision and bias values obtained in the validation to be related to the current concentration range of interest.

ADDITIONAL INFORMATION:

The lowest concentration in the range studied in method [1] is close to the limit of detection for the method. Therefore, when the lead levels to be determined are low, for example less than 0.05 mg/m^3, it is better to use graphite-chamber atomic absorption spectrometry, as an alternative analytical technique, in which case the recommended sampling volume can be substantially reduced [2][4][5].

REFERENCES

[1] OSHA. *ICP Analysis of Metal / Metalloid Particulates from Solder Operations*. Method No ID-206.

OTHER METHODS

[2] DFG. *Lead.* Analyses of Hazardous Substances in Air, Vol. 1, 177-187.

[3] NIOSH. *Lead by Flame AAS*. Manual of Analytical Methods, 4th ed., Method 7082.

[4] HSE. *Lead and inorganic compounds of lead in air.* Methods for the Determination of Hazardous Substances. MDHS 6/3.

[5] ISO 8518:2001 *Workplace air - Determination of particulate lead and lead compounds. Flame or electrothermal atomic absorption spectrometric method.*