

Appendix C:

Hazardous Property Assessment

The aim of this appendix is to:

- give advice on the hazards properties H1 to H14 identified in Annex III of the HWD;
- provide assessment methods and threshold concentrations for the hazards; and
- advise on which test methods should be considered.

The primary aim of the Hazardous Property Assessments is to assist in evaluating wastes covered by "*mirror entries*" and in determining whether they are hazardous waste or not.

Wastes identified as "*absolute entries*" in the EWC 2002 are hazardous waste. Assessment determines their appropriate hazards for Duty of Care purposes.

Appendix C:

C1 Assessment of Hazard H1: Explosive

C1.1 Definition of Explosive

Annex III of the HWD defines H1 "Explosive" as:

"substances or preparations which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene".

C1.2 Explosives Act 1875

Materials that are "explosives" within the meaning of the Explosives Act 1875, as amended, and any subsequent regulations issued under the Act, are not directive or controlled waste. The term "explosive" in the 1875 Act means:

- (1) *gunpowder, nitro-glycerine, dynamite, gun cotton, blasting powders, fulminate of mercury or of other metals, coloured fires and every other substance, whether similar to those above mentioned or not, used or manufactured with a view to produce a practical effect by explosion or a pyrotechnic effect;*

and includes

- (2) *fog-signals, fireworks, fuses, rockets, percussion caps, detonators, cartridges, ammunition of all descriptions, and every adoption or preparation of an explosive as defined above.*

The EWC 2002 contains the following absolute entries that relate directly to explosive wastes. Where wastes covered by these entries are regulated by the Explosives Act 1875, as amended, they would not be directive or controlled waste and are therefore excluded by Step 1 of the Hazardous Waste Assessment Methodology (see Chapter 3).

| | | |
|---|---|---|
| 16 01 | end-of-life vehicles from different means of transport (including off-road machinery) and wastes from dismantling of end-of-life vehicles and vehicle maintenance (except 13, 14, 16 06 and 16 08) | |
| 16 01 10* | explosive components (for example air bags) | A |
| 16 04 | Waste explosives | |
| 16 04 01* | waste ammunition | A |
| 16 04 02* | fireworks wastes | A |
| 16 04 03* | other waste explosives | A |
| However, other wastes may contain substances that are classified as explosive, for example picric acid from a laboratory, which could be covered by the mirror entry: | | |
| 16 05 | Gases in pressure containers and discarded chemicals | |
| 16 05 06* | laboratory chemicals, consisting of or containing dangerous substances, including mixtures of laboratory chemicals | M |

Controlled wastes that contain a substance classified as explosive need to be assessed for hazard H1.

C1.3 Risk Phrases

The ASL applies the category of danger "E" (explosive) to substances with risk phrases R1, R2 and R3. However, R1 relates to a particular circumstance, "explosive when dry", and so the hazard H1 is applied only in the case of substances with risk phrases R2 and R3:

R2 *Risk of explosion by shock, friction, fire or other sources of ignition*

Substances and preparations including certain organic peroxides but excepting those assigned R3.

R3 *Extreme risk of explosion by shock, friction, fire or other sources of ignition*

Substances and preparations which are particularly sensitive, such as picric acid salts or PETN (pentaerythritol tetranitrate).

Substances classified R3 are more sensitive than the explosive RDX (cyclotrimethylene trinitramine), and it is illegal to transport them. They are unlikely to be moved as hazardous waste.

C1.4 Related Risk Phrases

There are risk phrases that are not related directly to explosive properties, but rather to an ability to cause explosions in the presence of or in combination with other substances. Wastes containing substances with these risk phrases will be candidates for hazard H13, e.g. an R1 substance would not be hazardous when wet but it is clear that those responsible for managing the waste should be informed of its explosive properties in the dry state. The Approved Classification and Labelling Guide gives the following additional risk phrases:

R1 *Explosive when dry*

R4 *Forms very sensitive explosive metal compounds*

R5 *Heating may cause an explosion*

R6 *Explosive with or without contact with air*

R16 *Explosive when mixed with oxidising substances*

R18 *In use may form flammable/explosive vapour-air mixture*

R19 *May form explosive peroxides*

R44 *Risk of explosion if heated under confinement.*

C1.5 Limiting Concentrations

It is not possible to give a generic threshold for this hazard. Therefore controlled waste containing any concentration of substances with risk phrases R2 or R3 should be classified as hazardous waste by hazard H1 unless:

- it is known that other substances in the waste modify it to the extent that it is not explosive; and/or
- testing demonstrates that the waste is not more explosive than dinitrobenzene.

Many of the substances classified as explosive also display other hazards. For example, trinitrobenzene is classified as E in the ASL and carries risk phrase R2. This substance also carries the classification:

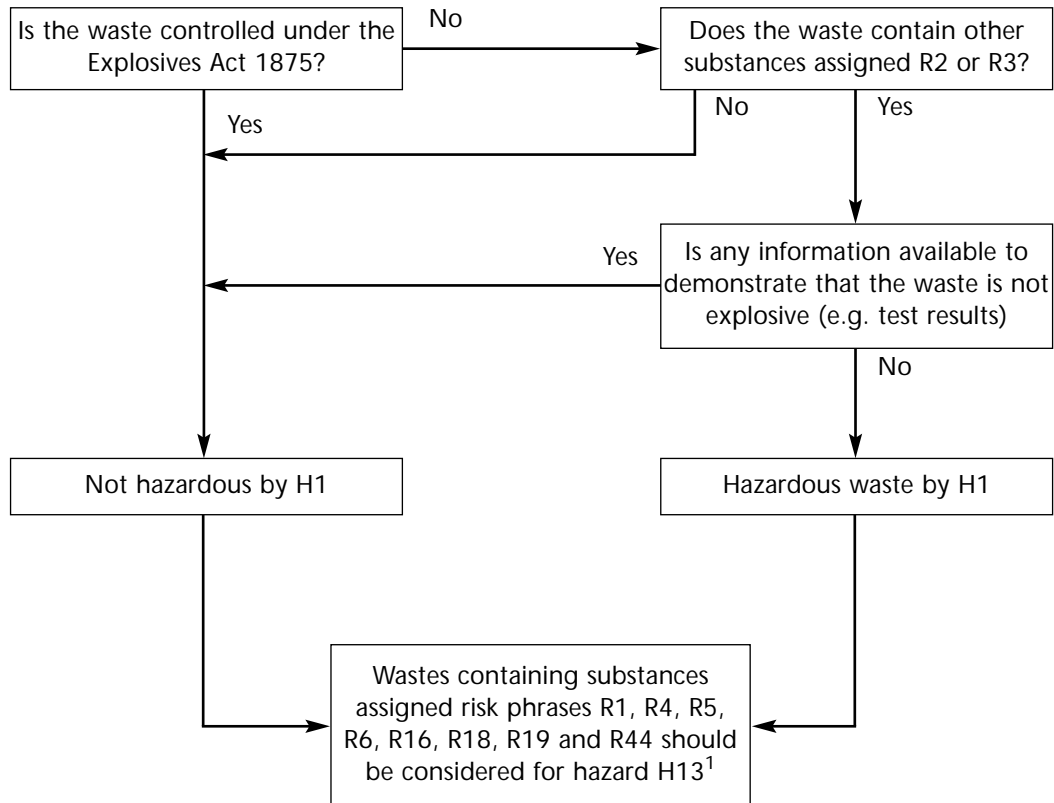
- T+ (very toxic); risk phrases R26, R27 and R28 (very toxic by inhalation, skin contact and by ingestion); and
- N (dangerous to the environment), risk phrases R51-53 (toxic to aquatic organisms and may cause long-term effects in the aquatic environment).

A waste containing $\geq 0.1\%$ of this substance will be hazardous by virtue of its toxicity (see Section C5).

C1.6 Decision Tree

Figure C1.1 sets out the assessment process for the Hazard H1.

Figure C1.1: Decision Tree for the Assessment of Hazard H1



Note:

¹ Except wastes covered by the Explosives Act 1875

C1.7 Test Methods

The EC test method which corresponds best to the definition of H1 "Explosive" is test method A14 from EC Directive 92/62/EEC.

There are significant safety hazards involved in carrying out the test on explosive substances. For these reasons, testing for hazard H1 should only be considered in exceptional circumstances, e.g. where non-test decisions have failed to correctly identify the waste as hazardous or not. Since hazard H1 is only likely to be considered for a number of potentially explosive wastes, it is equally possible to make a non-test decision and classify the waste as hazardous by H1.

C1.7.1 EC Test Method A14. Explosive Properties

Introduction

This method is designed to establish whether a substance or preparation presents a danger of explosion when submitted to the effect of a flame (thermal sensitivity) or to impact or friction (sensitivity to mechanical stimuli).

Principle of the Method

The method comprises three parts:

Test of Thermal Sensitivity. The method involves heating the substance or preparation in a steel tube, with various degrees of confinement being provided by nozzle-plates with different diameters of orifice. This determines whether the substance or preparation is liable to explode under conditions of thermal stress. The substance is considered explosive if an explosion occurs (i.e. the tube bursts into three or more fragments) within the fixed number of tests of thermal sensitivity.

Test of Mechanical Sensitivity (with respect to shock). The method involves subjecting the substance or preparation to the shock from a mass dropped from a specified height. The substance is considered explosive if the results show an explosion (bursting into flame is equivalent to explosion) occurring at least once in six tests with the specified impact apparatus, or if the sample is more sensitive than 1,3-dinitrobenzene in an alternative impact test.

Test of Mechanical Sensitivity (with respect to friction). The method involves subjecting the solid or pasty substance to friction between standard surfaces under specified conditions of load and relative motion. The substance is considered explosive if the results show an explosion (crepitation or bursting into flame is equivalent to explosion) occurring at least once in six tests with the specified friction apparatus, or if the sample is more sensitive than 1,3-dinitrobenzene in an alternative friction test.

Comments

The test method yields data for the likelihood that certain common stimuli will initiate an explosion. It is not intended to ascertain whether or not a substance or preparation is capable of exploding under any conditions.

The method is appropriate for the conditions specified in Directive 84/449/EEC. The tests are irrelevant when available thermodynamic information (e.g. heat of formation, heat of decomposition or absence of certain reactive groups in the structural formula¹) establishes beyond reasonable doubt that the substance or preparation is incapable of decomposing, forming gases and releasing heat very rapidly (i.e. the material does not present any risk of explosion).

The method is not definitive. It comprises a number of chosen types of specified apparatus which are widely used internationally and which usually give meaningful results. The person conducting the tests may elect to use alternative apparatus in the three methods specified, providing it can be justified scientifically and the apparatus is recognised internationally. In this case he must determine the correlation of his results with those obtained with the specified apparatus.

To avoid injury to the experimenter a preliminary screening test is necessary to establish safe conditions for the performance of the three tests and so ascertain if the prescribed sensitivity tests should be performed with special precautions. For the screening test very small samples (circa 10 mg) of the substance or preparation should be subjected to heating without confinement in a gas flame, to impact in any convenient form of apparatus and to friction by the use of a mallet against an anvil or any form of friction machine.

The reader should refer to the full test method for details on apparatus and reference substance specifications in addition to the requirements for test conditions, test performance, result reporting and evaluation.

¹ Bretherick, L. 1979. Handbook of Reactive Chemical Hazards. Butterworths, pp. 60 to 63.

Appendix C:

C2 Assessment of Hazard H2: Oxidising

C2.1 Definition of Oxidising

Annex III of the HWD defines H2 "Oxidising" as:

"substances and preparations which exhibit highly exothermic reactions when in contact with other substances, particularly flammable substances"

C2.2 Risk Phrases

A waste may exhibit the hazard "oxidising" (H2) if it contains a substance assigned one of the following risk phrases:

R7 *May cause fire*

Organic peroxides which have flammable properties even when not in contact with other combustible material.

This risk phrase is most commonly attributed to organic peroxides. These have flammable properties even when not in contact with other combustible material, due to the chemical structure of the compound, which combines a flammable hydrocarbon functional group with a peroxide functional group.

R8 *Contact with combustible material may cause fire*

Other oxidising substances and preparations, including inorganic peroxides, which may cause fire or enhance the risk of fire when in contact with combustible material.

R9 *Explosive when mixed with combustible material*

Other substances and preparations, including inorganic peroxides which become explosive when mixed with combustible materials, e.g. certain chlorates.

Substances which are oxidising can be distinguished from substances which are flammable: oxidising substances can initiate combustion in the absence of air.

The risk phrase R16, *Explosive when mixed with oxidising material*, is clearly included within the broad definition of H2. The only substance in the ASL defined as R16 is red phosphorus. Red phosphorus is, however, also listed as R11, highly flammable, and is therefore adequately described and classified by H3A (third indent). R16 should not be considered to apply to Hazard H2 specifically, but should be considered under H13 (see Section C13.2).

C2.3 Limiting Concentrations

There is no single limiting concentration applicable to substances that exhibit Hazard H2. This is because the potency of the substance as an oxidiser is dependent upon, among other criteria:

- the chemical structure of the substance;
- the percentage of oxygen available for reaction.

The hierarchy for deciding on threshold limiting concentrations should be as follows:

- substances listed on the ASL with specific concentration limits;
- organic peroxides, for which concentration limits may be calculated;
- inorganic and other oxidisers, for which testing is the only option.

C2.4 Organic Peroxides

Organic peroxides² combine the properties of an oxidiser and a combustible substance in one molecule, and have the following generic limiting concentrations attributed to them. Any waste containing organic peroxides will be classified as hazardous by H2 if the waste contains:

- more than 5% by weight of organic peroxides;
- more than 0.5% available oxygen from the organic peroxides, when containing more than 5% hydrogen peroxide.

The method for calculating the amount of available oxygen from the organic peroxide is set out below:

The available oxygen content, O_i (%) of an organic peroxide i , is given by:

$$O_i (\%) = 16 \times (n_i \times c_i / m_i)$$

Where 16 = gram molecular mass of the available oxygen of the peroxide functional group -O-O-.

n_i = number of peroxide groups per molecule of organic peroxide i .

c_i = concentration (mass %) of organic peroxide i in the waste.

m_i = gram molecular mass of organic peroxide i .

Given point (ii) above, it is possible to identify the concentration of organic peroxides that would make a waste hazardous when in the presence of more than 5% hydrogen peroxide by rearranging the above formula as follows:

$$c_i = (O_i \times m_i) / (16 \times n_i)$$

An example calculation is in Box C2.1.

Box C2.1: Calculating concentration of organic peroxide required to make a waste hazardous

Example calculation for methyl ethyl peroxide

Methyl ethyl peroxide has the chemical formula $C_2H_5-O-O-CH_3$ and molecular mass 76 g. There is one peroxide functional group present, therefore, $n_i = 1$.

The limiting concentration for organic peroxides is one which would give rise to an available oxygen concentration of 0.5%, therefore, $O_i = 0.5$. The concentration c_i which would give rise to this is:

$$c_i = (O_i \cdot m_i) / (16 \cdot n_i)$$

$$c_i = (0.5 \cdot 76) / (16 \cdot 1)$$

$$c_i = 2.4$$

Therefore a waste would be hazardous by H2 if:

- the methyl ethyl peroxide concentration exceeded 5%; or
- the methyl ethyl peroxide concentration exceeded 2.4% in the presence of >5% hydrogen peroxide.

² Generic formula R-OO-R, e.g. methyl ethyl peroxide $C_2H_5-O-O-CH_3$.

C2.5 Other R7, R8 and R9 Oxidisers

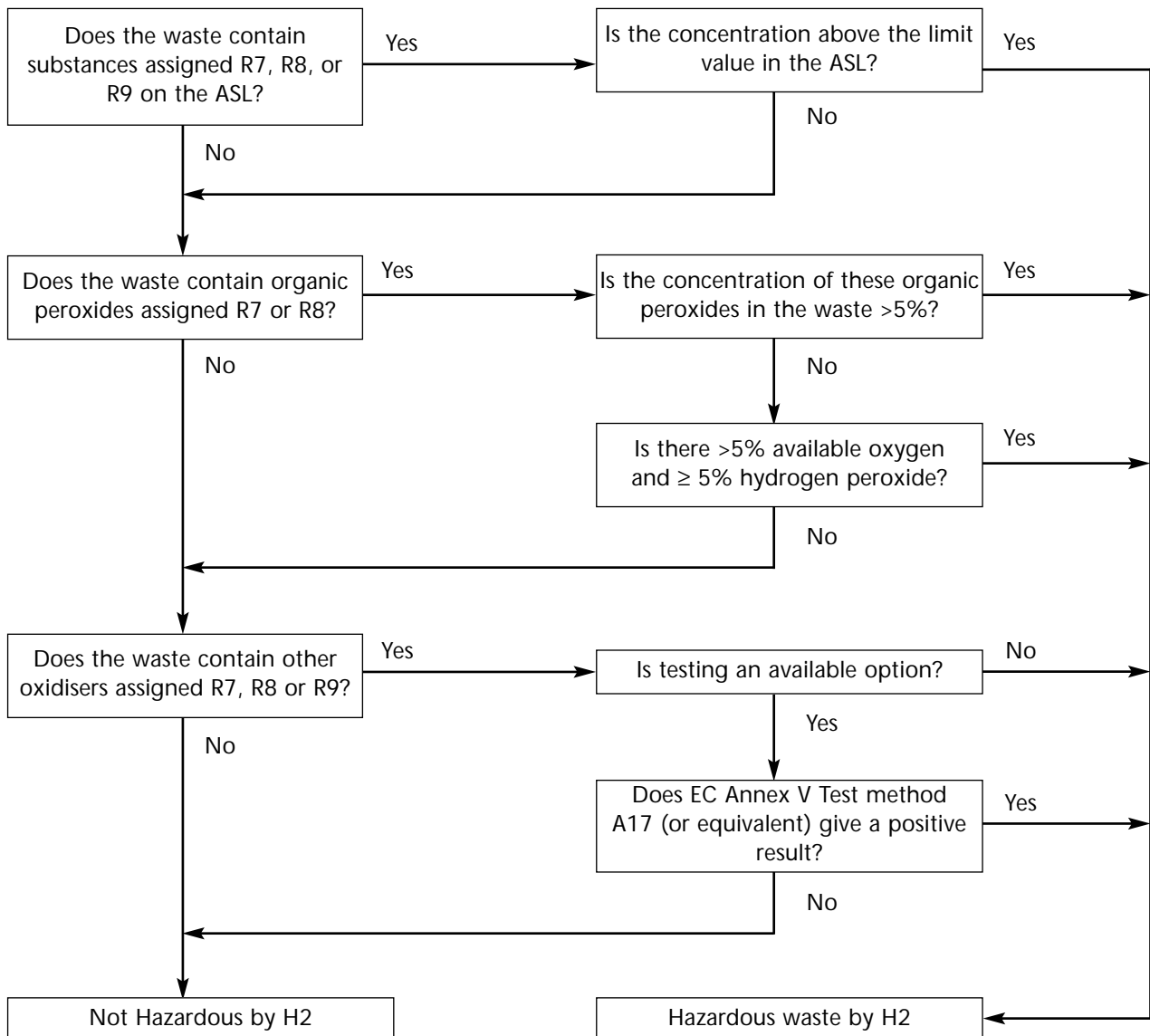
Limiting concentrations for the bulk of the substances classified by these risk phrases remain undetermined or are commercially confidential. The reactivity and free oxygen cannot be determined from the structure, and therefore calculating limiting concentrations is not possible. In the case of inorganic oxidisers testing is required.

Primary producers generally chemically degrade inorganic oxidisers in a controlled manner, before disposal. The majority of oxidiser waste is created by secondary users, and, if not destroyed, all inorganic oxidants are considered dangerously reactive. In particular perchlorates and bromates can react explosively when mixed with combustible materials (R9).

C2.6 Decision Tree

Figure C2.1 sets out the assessment process for the Hazard H2.

Figure C2.1: Decision Tree for the Assessment of Hazard H2



C2.7 Test Methods

The approved test methods are shown in Table C2.1.

Table C2.1: Hazard H2, associated risk phrases and relevant test methods

| Hazard | Phase | Risk phrase | Test |
|--------|---|-------------|---|
| H2 | Solid (not explosive, highly flammable, organic peroxides or combustible) | R7, R8 | Directive 92/69/EEC, Test Method A17 |
| | Organic peroxides | R7, R8, R9 | Use calculation method as no test available |
| | Liquids and oxidising materials not covered by the classes listed above | R7, R8, R9 | No test available |

The EC approved Annex V test method A17, described below, and the test in HSE L88, are not applicable to the following:

- liquids or gases
- explosive or highly flammable substances
- organic peroxides
- combustible solids liable to melt under the conditions of the test.

Although there is no test applicable to organic peroxides, there is a generic threshold limit, and the approved calculation method for determining when they are oxidising is described in Section 3.5. There is no currently recommended or agreed standard test for liquid oxidisers. Advice for specific testing of liquid oxidisers should be sought from the Health and Safety Executive Health Directorate, Industrial Chemicals Unit, Magdalen House, Stanley Precinct, Bootle, Merseyside L20 3QZ (0151 951 4000).

Waste materials exhibit considerable variability in composition and the approved test method is not applicable to all oxidising materials. In addition, there are significant safety hazards involved in carrying out the test on oxidising substances. For these reasons, testing for hazard H2 should only be considered in exceptional circumstances, e.g. where non-test decisions have failed to correctly identify the waste as hazardous or not.

C2.7.1 EC Test Method A17: Oxidising Properties (solid)

The test method which corresponds best to the definition of the hazard is test method A17 from EC Directive 92/69/EEC. This test method is not applicable to liquids and gases, explosive or highly flammable substances, organic peroxides or to combustible solids liable to melt under the conditions of the test.

Introduction

It is useful to have preliminary information on potentially explosive properties and toxicity of the substance before performing this test. This test is irrelevant when examination of the structural formula establishes beyond reasonable doubt that the substance or preparation is not capable of reacting exothermically with a combustible material.

Principle of Method

In order to ascertain if the test should be performed with special precautions, a preliminary test should be performed. A preliminary test establishes an oxidation hazard if the test substance reacts vigorously. When this is not the case, the substance or preparation should then be subject to a full test as summarised below.

The full test method involves the burning of a range of mixtures formed from the test substance and a defined combustible substance. Each mixture from the range is then formed into a pile and ignited at one end. The maximum burning rate determined is compared with the maximum burning rate of the reference mixture cellulose and barium nitrate. The substance is considered to be oxidising when the maximum burning rate of the mixtures to be tested is higher than or equal to the maximum burning rate of the reference mixture.

The full method provides explicit details of preparation of the test substance and the barium nitrate and cellulose utilised as reference substances. The method presents clear guidelines on apparatus, test performance, quality criteria, reporting and evaluation of the results.

C2.7.2 Alternative Methods

Similar tests are used for classification under the Transport of Dangerous Goods Regulations; details and guidance on the tests can be obtained from the Health and Safety Executive.

Appendix C:

C3 Assessment of Hazard H3: Flammable

C3.1 Definition

Hazard H3 is divided into two sections

- highly flammable (H3A)
- flammable (H3B).

H3A is further divided into five sub-sections with these sub-sections referred to as H3A (first–fifth indents) or H3A(i–v).

Annex III of the HWD defines H3A “Highly flammable” as:

- liquid substances and preparations having a flash point below 21°C (including extremely flammable liquids), or*
- substances and preparations which may become hot and finally catch fire in contact with air at ambient temperature without application of energy, or*
- solid substances and preparations which may readily catch fire after brief contact with a source of ignition and which continue to burn or to be consumed after the removal of the ignition source, or*
- gaseous substances and preparations which are flammable in air at normal pressure, or*
- substances or preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.*

Annex III of the HWD defines H3B “Flammable” as:

“Liquid substances and preparations having a flash point equal to or greater than 21°C and less than or equal to 55°C”.

C3.2 Risk Phrases

A waste possessing H3A(i–v) or H3B is likely to contain a substance with one or more of the following risk phrases.

R10 *Flammable*

For liquid substances and preparations having a flashpoint equal to or greater than 21°C, and less than or equal to 55°C.

R11 *Highly Flammable*

Solid substances and preparations which may readily catch fire after brief contact with a source of ignition and which continue to burn or to be consumed after removal of the source of ignition; or

Liquid substances having a flashpoint below 21°C but which are not extremely flammable.

R12 *Extremely Flammable*

Liquid substances and preparations which have a flashpoint lower than 0°C and a boiling point (or in case of a boiling range the initial boiling point) lower than or equal to 35°C; or

Gaseous substances and preparations which are flammable in contact with air at ambient temperature and pressure.

R15 *Contact with water liberates extremely flammable gases*

Substances and preparations, which, in contact with water or damp air, evolve extremely flammable gases in dangerous quantities, at a minimum rate of 1 litre per kg per hour.

R17 *Spontaneously flammable in air*

Substances and preparations which may become hot and finally catch fire in contact with air at ambient temperature without any input of energy.

Flammability may not be the only hazard possessed by a waste, but it is important, and should always be recorded. Classification as flammable may be necessary to meet the legal requirements for carriage of the waste.

C3.3 Related Risk Phrases

The following are related risk phrases:

R14 *Reacts violently with water*

R18 *In use may form flammable/explosive vapour-air mixture*

R30 *Can become highly flammable in use*

These risk phrases are only associated with waste exhibiting other hazards, and will not constitute hazardous waste in isolation. Wastes containing these risk phrases will be candidates for hazard H13 (see Appendix C13).

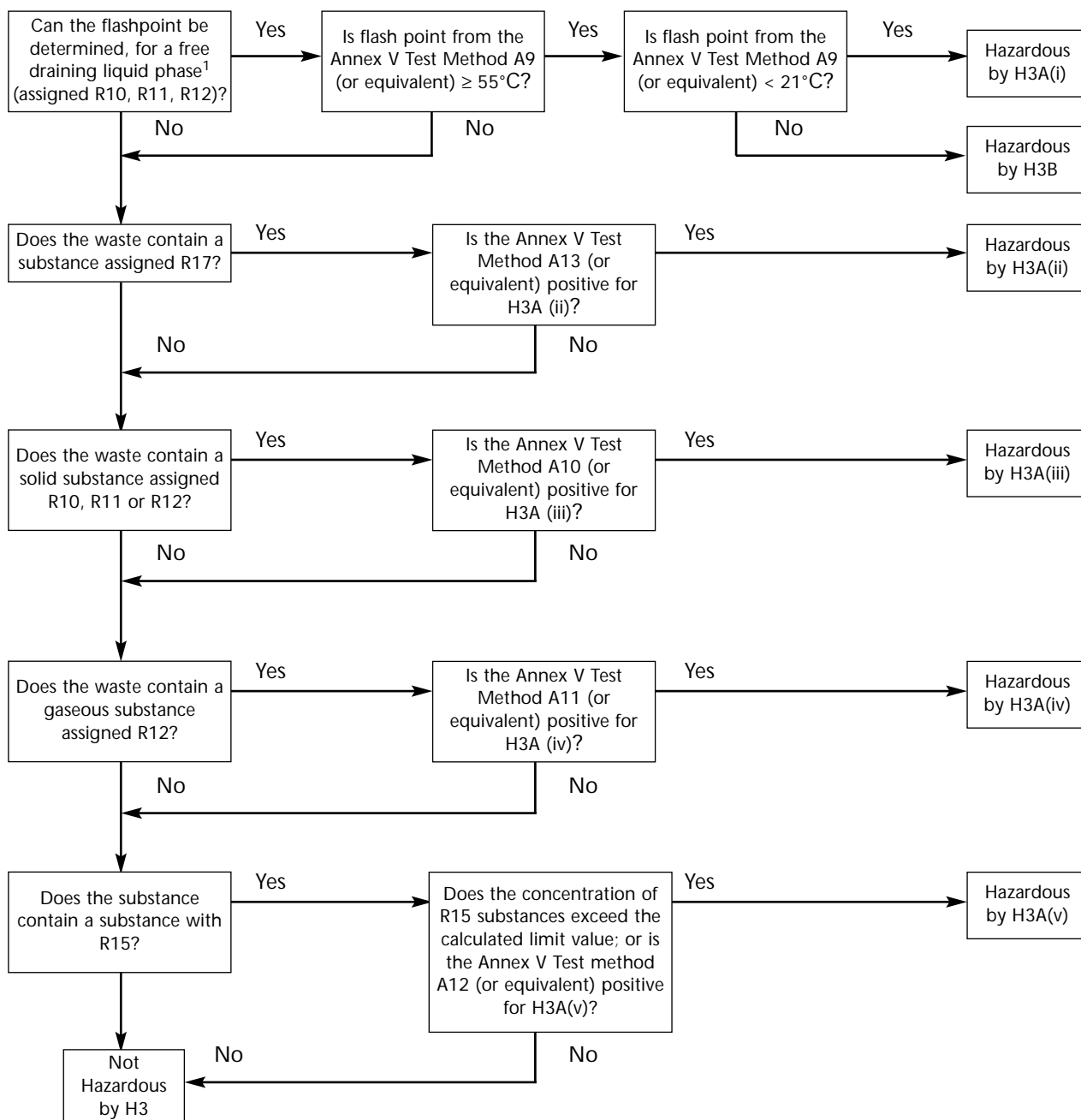
C3.4 Combined Risk Phrases

Any combination of risk phrases including R10, R11, R12, R15 or R17 indicates the potential to exhibit hazard H3. Related risk phrases must be in combination with the above to indicate the potential for hazard H3.

C3.5 Decision Tree

If substances are present in the waste which have any of the risk phrases R10, R11, R12, R15 or R17, the waste will generally require testing to determine whether it exhibits the particular hazard, with the exception of H3A(v) which should be determined using a calculation method (see Section C3.5.1). Figure C3.1 sets out the assessment process for the Hazard H3.

Figure C3.1: Decision Tree for the Assessment of Hazard H3



Note:

¹ A free draining liquid phase is a liquid that can be poured or decanted from a waste.

Note also that:

Many solid substances classified R17, which have the potential for hazard H3A(ii), are also R15 (particularly in powder form), which makes them candidates for H3A(v) as well.

Dilution of low flashpoint liquids in a solid or liquid matrix will raise the flashpoint until, at some stage, the dilution effect will render the waste non-hazardous by H3. Unless otherwise known, testing must be carried out on:

- the mixture;
- the separate phases in the case of two-phase solid/freely draining liquid mixtures, e.g. toluene impregnated soils; or
- the liquid extracted from absorbents/rags by physical or mechanical means.

C3.5.1 Calculation Method for Hazard H3A(v)

This hazard can be determined by calculation or by testing. If information on the composition of the waste is available the calculation method should be used; otherwise EC standard test method A12 or equivalent should be used (see Section C3.6).

The first step in the calculation method is to determine whether the waste contains any of the substances which are classified by the following risk (or combined risk) phrases:

R15 *Contact with water liberates extremely flammable gas*

R14/15 *Reacts violently with water, liberating extremely flammable gas*

R15/29 *Contact with water liberates toxic, extremely flammable gas*

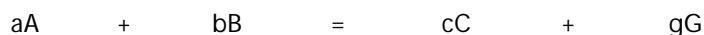
To show this hazard property, the waste should be capable of releasing a highly flammable gas at a rate in excess of 1 m³ gas per tonne of waste per hour (or at an equivalent rate). It should be assumed that if a substance is classified by any of the above risk phrases, or could be classified by any of these risk phrases, this criterion has already been met.

From the listing of substances on the ASL which exhibit this hazard property, the extremely flammable gases which could be released by chemical reaction with water appear to be limited to the following:

| | | |
|--------------------|-------------------------------|-------------------|
| hydrogen | H ₂ | by R15 and R14/15 |
| ethane | C ₂ H ₆ | by R14/15 |
| ethyne (acetylene) | C ₂ H ₂ | by R15 |
| phosphine | PH ₃ | by R15/29 |

The waste producer should also consider what other solid substances in his waste could break down to give off extremely flammable gases, and carry out the assessment set out in Box H3.1.

1. Write a balanced equation for the reaction that produces the gas. The general form of this equation should be as follows:



where: A, B, C and G are the products and reactants; and

a, b, c and g are the stoichiometric ratios between the products and reactants.

2. Attribute molecular weights and stoichiometric ratios to the substances in the equation.
3. Divide (a x molar weight of A) by (g x 22.4 [the volume of 1 mol of gas at 25°C and 1 atmosphere pressure (STP)]). This gives the mass of reactant A that will evolve 1 litre of gas G.
4. The limiting concentration for the substance in the waste with the potential to show hazard H3A(v) is this amount (in grams) divided by 1,000 (to convert to kg) and multiplied by 100 (to give % by weight). The same calculation can be used to determine hazard H12.

Example Calculation – The main constituents which may make aluminium drosses and slags hazardous, covered by “*mirror entry*” 10 08 10*, are aluminium, aluminium nitride, aluminium carbide. Aluminium powder is classified F: R15 and R10, with aluminium carbide assigned R15. Applying this calculation method to the aluminium drosses and slags gives the following threshold limits. (Note: other constituents may make the aluminium drosses and slags hazardous by H12, see Appendix C12.)

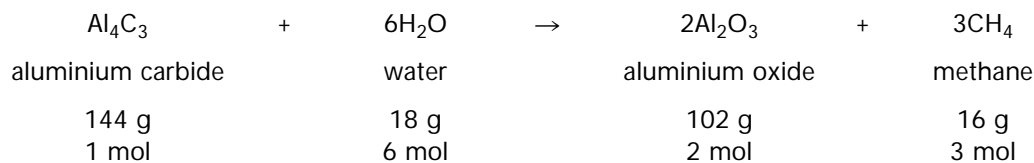
Aluminium powder (R15) giving rise to hazard H3A(v)



Limiting concentration of aluminium powder in waste

$$= [(2 \times 27) / (3 \times 22.4)] / 1,000 \times 100 = 0.08\% \approx 0.1\%$$

Aluminium carbide (R15) giving rise to hazard H3A(v)



Limiting concentration of aluminium carbide in waste

$$= [144 / (3 \times 22.4)] / 1,000 \times 100 = 0.21\% \approx 0.2\%$$

Threshold limits for certain ASL listed substances, for Hazard H3A(v), have been derived using the assessment methodology and are set out in Table C3.1. It should also be noted that a substance exhibiting R15/29 also has the potential to exhibit hazard H12, and the threshold limit for that hazard will be the same as that established for H3A(v).

Table C3.1: Examples of substances which may cause a waste to exhibit hazard H3A(v) (Classification by risk phrases R15, R14/15 and R15/29)

| Substance name | Risk phrases | Equation | Threshold Conc. % |
|---|--------------|--|-------------------|
| Lithium | R14/15 | $2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2$ | 0.06 |
| Sodium | R14/15 | $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$ | 0.2 |
| Magnesium powder (pyrophoric) | R15-17 | $\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{H}_2$ | 0.1 |
| Aluminium powder (pyrophoric) | R15-17 | $2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2$ | 0.08 |
| Aluminium powder (stabilised) | R15 | | |
| Potassium | R14/15 | $2\text{K} + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{H}_2$ | 0.4 |
| Calcium | R15 | $\text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{H}_2$ | 0.2 |
| Zinc powder/dust (pyrophoric) | R15-17 | $\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2 + \text{H}_2$ | 0.3 |
| Zinc powder/zinc dust | R15 | | |
| Zirconium powder (pyrophoric) | R15-17 | $\text{Zr} + 4\text{H}_2\text{O} \rightarrow \text{Zr}(\text{OH})_4 + 2\text{H}_2$ | 0.2 |
| Zirconium powder (non pyrophoric) | R15 | | |
| Aluminium lithium hydride | R15 | $\text{LiAlH}_4 + \text{H}_2\text{O} \rightarrow \text{LiAl}(\text{OH})_4 + 4\text{H}_2$ | 0.04 |
| Sodium hydride | R15 | $\text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$ | 0.1 |
| Calcium hydride | R15 | $\text{CaH}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2\text{H}_2$ | 0.1 |
| Calcium carbide | R15 | $\text{CaC}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$ | 0.3 |
| Calcium phosphide | R15/29 | $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{PH}_3 + 3\text{Ca}(\text{OH})_2$ | 0.4 |
| Aluminium phosphide | R15/29 | $\text{AlP} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + \text{Al}(\text{OH})_3$ | 0.3 |
| Magnesium phosphide | R15/29 | $\text{Mg}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{PH}_3 + 3\text{Mg}(\text{OH})_2$ | 0.3 |
| Trizinc diphosphide | R15/29 | $\text{Zn}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{PH}_3 + 3\text{Zn}(\text{OH})_2$ | 0.6 |
| Trichlorosilane | R14-17 | $\text{Cl}_3\text{HSi} + \text{H}_2\text{O} \rightarrow \text{Cl}_3(\text{OH})\text{Si} + \text{H}_2$ | 0.6 |
| Diethyl (ethyl-dimethyl-silanolato) aluminium | R14/15, 17 | $(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_3)_2\text{C}_2\text{H}_5\text{Al} + 2\text{H}_2\text{O} \rightarrow 2\text{C}_2\text{H}_6 + \text{Al}(\text{OH})_2\text{Si}(\text{CH}_3)_2\text{C}_2\text{H}_5$ | 0.4 |

Notes:

R15 Contact with water liberates extremely flammable gases

R14/15 Reacts violently with water, liberating extremely flammable gas

R15/29 Contact with water liberates toxic, extremely flammable gas (may also exhibit hazard H12)

R17 Spontaneously flammable in air

C3.6 Test Methods

Unless otherwise known, test procedures for flammability are recommended for all except for hazard H3A(v) which should be assessed using the calculation method in Section 3.5.1. The approved test methods for the determination of flammable properties are set out in Table C3.2. The appropriate hazard may be identified following the outcome of the test.

Table C3.2: Hazard H3 with associated risk phrases and relevant approved test methods

| Hazard | Phase | Risk phrase | Test and Reference |
|----------|-----------------|------------------|--|
| H3A(i) | liquid | R11 and some R10 | Directive 92/69/EEC, Test Method A9 |
| | liquid | R12 | Directive 92/62/EEC, Test Method A11 |
| H3A(ii) | solid or liquid | R17 | Directive 92/62/EEC, Test Method A13. |
| H3A(iii) | solid | R11 | Directive 92/62/EEC, Test Method A10. |
| H3A(iv) | gas | R12 | 1. Directive 92/62/EEC, Test Method A11. 2. Directive 92/62/EEC, Test Method A15 is a useful adjunct to test A11. |
| H3A(v) | solid/liquid | R15 | Directive 92/62/EEC, Test Method A12. |
| H3B | liquid | R10 and some R11 | Directive 92/62/EEC, Test Method A9. |

Similar tests are used for classification under the Transport of Dangerous Goods Regulations; details and guidance on the tests can be obtained from the Health and Safety Executive.

C3.6.1 EC Test Method A9 (flashpoint) for Hazard H3A (first indent) and H3B

Introduction

This test is for flashpoint. It is useful to have preliminary information on the flammability of the substance to perform this test. The test procedure is only applicable to liquid substances, whose vapours can be ignited by ignition sources. The test methods described in this text are only reliable for flashpoint ranges which are specified in the individual methods.

The flashpoint is the lowest temperature, corrected to a pressure of 101 325 kPa (1 atmosphere) at which a liquid evolves vapours, under the conditions defined in the test method, in such an amount that a flammable vapour/air mixture is produced in the test vessel.

Principle of the method

The substance is placed in a test vessel which is progressively heated or cooled to the test temperature according to the procedure described in the individual test method. Ignition trials are carried out in order to ascertain whether or not the sample flashed at that temperature. Reference substances should be used to calibrate the method from time to time and to offer a chance to compare results when another method is applied.

Sensitivity and reproducibility vary according to the test method used. The specificity of some test methods is limited to certain flashpoint ranges and subject to substance-related data (e.g. high viscosity).

For full details on the performance of the test refer to the following methods.

Equilibrium method: see the following ISO standards.

- ISO 1516
- ISO 3680
- ISO 1523
- ISO 3679.

Non-equilibrium method: refer to the following methods.

- Abel apparatus: BS 2000 part 170, NF M07-011, NF T66-009
- Abel-Pensky apparatus: (EN 57), DIN 51755 part 1 (5 - 65°C), and part 2 (<5°C), NF M07-036
- Tag apparatus: ASTM D 56
- Pensky-Martens apparatus: ISO 2719, EN 11, DIN 51758, ASTM D 93, BS 2000-34, NF M07-019
- For viscous liquids (paints, gums and similar) containing solvents, only apparatus and test methods suitable for determining the flashpoint of viscous liquids may be used: see ISO 3679, ISO 3680, ISO 1523, DIN 53213 part 1.

C3.6.2 Summary of EC Test Method A13 (Pyrophoric Properties of Solids and Liquids) for Hazard H3A (second indent)

Introduction

It is useful to have preliminary information on the auto-flammability of a substance. The test procedure is only applicable to solid and liquid substances which in small amounts will ignite spontaneously a short time after coming into contact with air at room temperature (circa 20°C).³

Substances not covered by this test method are those which need hours or days at room temperature before self-ignition occurs, or those which need to be exposed to considerably higher temperature before self-ignition occurs.

The auto-flammability of liquids may also need to be tested following the result of EC Test Method A15 Auto-ignition temperature (liquids and gases) for hazard H3A (fourth indent) (see Section C3.6.4 below.)

Principle of the method

The substance, whether solid or liquid, is added to an inert carrier and brought into contact with air at ambient temperature for a period of five minutes. If liquid substances do not ignite they are absorbed onto filter paper and exposed to air at ambient temperature (circa 20°C) for five minutes. If the substance ignites within five minutes when added to an inert carrier and exposed to air, or a liquid substance chars or ignites a filter paper within five minutes when added and exposed to air, it is considered to be pyrophoric and therefore highly flammable.

³ NF T 20-039 (SEPT 85). Chemical products for industrial use. Determination of the spontaneous flammability of solids and liquids.

Testing can be discontinued as soon as a positive result occurs in any of the tests: because safety is at stake, a single positive result is sufficient for the substance to be considered highly flammable.

The full test method should be referred to for complete details on test performance.

C3.6.3 EC Test Method A10 (Flammability (solids)) for Hazard H3A (third indent)

Introduction

It is useful to have preliminary information on any potentially explosive properties of the substance before performing this test. This test should only be applied to powder, granular and paste-like substances.⁴

In order to include only those substances which burn rapidly or those whose burning behaviour is in any way especially dangerous, only substances whose burning velocity exceeds a certain limiting value are considered to be highly flammable.

It can be especially dangerous if incandescence propagates through a metal powder because of the difficulties in extinguishing the fire. Metal powders should be considered highly flammable if they support spread of incandescence throughout the mass within a specified time.

Principle of the method

The substance is formed into an unbroken strip or powder train of specified length and a preliminary screening test performed to determine if, on ignition by a gas flame, propagation by burning with flame or smouldering occurs. If the propagation over a specified proportion of the train occurs within a specified time the full test programme to determine the burning rate is carried out.

Powdery, granular or pasty substances are to be considered as highly flammable when in one of the test runs they give a burning time as less than 45 seconds. Powders of metals or metal alloys are considered to be highly flammable when they can be ignited and the flame or the zone of reaction spreads over the whole sample in 10 minutes or less.

The full test method should be referred for complete details on test apparatus, test performance and results evaluation.

C3.6.4 EC Test Method A15 (Auto-ignition Temperature (liquids and gases)) for Hazard H3A (fourth indent)

Introduction

It is useful to have preliminary information on the auto-flammability of a substance. Explosive substances and substances which ignite spontaneously in contact with air at ambient temperature should not be submitted to this test. The test procedure is applicable to gases and volatile liquid substances whose vapours can be ignited by a hot surface in the presence of air, by a hot surface.

Auto-ignitability is expressed in terms of auto-ignition temperature, which is the lowest temperature at which the test substance will ignite when mixed with air under the conditions defined in the test method.

Principle of the method

The method determines the minimum temperature of the inner surface of an enclosure that will result in ignition of a gas, vapour or liquid injected into the enclosure. For performance of the test refer to the following methods: IEC 79-4, DIN 51794, ASTM-E 659-78, BS 4056, NF T 20-037. Reference substances are cited and should primarily serve to check the performance of the method from time to time and allow comparison with results from other methods. The reproducibility varies according to the range of self-ignition temperatures and the test method used. The sensitivity and specificity will also vary with the chosen test method.

⁴ NF T 20-042 (SEPT 85). Chemical products for industrial use. Determination of the flammability of solids.

C3.6.5 EC Test Method A11 (Flammability (gases)) for Hazard H3A (fourth indent)

Introduction

This method allows a determination of whether gases mixed with air at room temperature and atmospheric pressure are flammable, and if so over what range of concentrations. Mixtures of increasing concentrations of the test gas with air are exposed to an electrical spark and it is observed whether ignition occurs.

Principle of method

The range of flammability is the range of concentration between the lower and upper explosive limits (LEL and UEL). The LEL and UEL are those limits of concentration of the flammable gas in admixture with air at which propagation of a flame does not occur. The occurrence of flame propagation is the only relevant information data for the determination of this property.⁵

The test vessel is an upright glass cylinder fitted with a pressure-release opening. Ignition electrodes send a spark generated from a high voltage transformer. The apparatus is shielded to restrict any explosion damage. Using proportioning pumps, a known concentration of gas in air is introduced into the glass cylinder and the spark is passed through the mixture. It is observed whether or not a flame detaches itself from the ignition source and propagates independently.

Refer to the full method in the Directive for specification of test apparatus, test conditions and performance.

C3.6.6 EC Test Method A12 (Flammability (contact with water)) for Hazard H3A (fifth indent)

Introduction

This test method can be used to determine whether the reaction of a substance with water or damp air evolves gas or gases that are highly flammable.⁶ The method can be applied to both solid and liquid substances; however, it is not applicable to substances which spontaneously ignite when in contact with air.

Principle of the method

The substance is tested according to the step by step sequence outlined below. The initial steps in the method are to establish whether the substance reacts violently with water; if it is known that it does not then performance of these parts of the method not required. The substance is considered hazardous if spontaneous ignition occurs in any step of the test procedure, or evolution of flammable gas evolves at a rate greater than 1 litre/kg of substance per hour.

Step 1. The test substance is placed in a trough containing distilled water at room temperature and it is noted whether or not the evolved gas ignites.

Step 2. The test substance is placed on a filter paper floating on the surface of a dish containing distilled water at room temperature and it is noted whether or not the evolved gas ignites. The filter paper is merely to keep the substance in one place to increase the chances of ignition.

Step 3. The test substance is made into a small pile and a few drops of water are added to the pile and it is noted whether or not the evolved gas ignites.

Step 4. The test substance is mixed with distilled water at 20°C and the rate of evolution of gas is measured over a period of seven hours at one-hour intervals. If the rate of evolution is erratic, or is increasing, after seven hours, the measuring time should be extended to a maximum time of five days. The test may be stopped if the rate at any time exceeds 1 litre per kg per hour.

For the details and specifications of test apparatus and performance the full method should be referred to.

Alternative Methods

Similar tests are used for classification under the Transport of Dangerous Goods Regulations; details and guidance on the tests can be obtained from the Health and Safety Executive.

⁵ NF T 20-041 (SEPT 85). Chemical products for industrial use. Determination of the spontaneous flammability of gases.

⁶ NF T 20-040 (SEPT 85). Chemical products for industrial use. Determination of the spontaneous flammability of gases formed by the hydrolysis of solids and liquids.

Appendix C:

C4 Assessment of Hazards H4/H8: Irritant and Corrosive

C4.1 Definition

"Irritant" (H4) and "Corrosive" (H8) hazards are linked because they both refer to the potential for harm or damage to tissue.

Annex III of the HWD defines H4, "Irritant" as:

"Non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation".

Annex III of the HWD defines H8, "Corrosive" as:

"substances and preparations which may destroy living tissue on contact".

Preparations containing corrosive substances can exhibit either corrosive or irritant properties dependant upon concentration. However, substances classified as irritants can not become corrosive.

C4.2 Risk Phrases

In the following list of the risk phrases associated with the hazards irritant and corrosive, R34 and R35 are risk phrases associated with corrosive, the others relate to irritant:

R35 *Causes severe burns*

This risk phrase is assigned to substances which, when applied to healthy intact animal skin, cause full thickness destruction of skin tissue in up to three minutes exposure or to substances where this result can be predicted.

R34 *Causes burns*

This risk phrase is assigned to substances which, when applied to healthy intact animal skin, cause full thickness destruction of skin tissue in up to four hours exposure; or to substances where this result can be predicted. Organic hydroperoxides are assigned this risk phrase unless there is evidence to the contrary.

R36 *Irritant to eyes*

This risk phrase is assigned to substances if, when applied to the eye of an animal, significant ocular lesions occur within 72 hours after exposure and persist for at least 24 hours. Organic peroxides are assigned this risk phrase unless there is evidence to the contrary.

R37 *Irritant to respiratory system*

This risk phrase is assigned to substances and preparations which cause serious irritation to the respiratory system; the conclusion is normally based on:

- a) practical observations in humans;
- b) positive results from appropriate animal tests.

R38 *Irritant to skin*

This risk phrase is assigned to substances which cause significant inflammation of the skin which persists for at least 24 hours after an exposure period of up to four hours (based on the rabbit cutaneous irritation test method in Annex V of Directive 67/548/EEC). Organic peroxides are assigned this risk phrase unless there is evidence to the contrary.

R41 *Risk of serious damage to eyes.*

This risk phrase is assigned to substances which, when applied to the eye of an animal, cause severe ocular lesions within 72 hours after exposure if the lesions are present 24 hours or more after the instillation of the test material.

C4.3 Combined Risk Phrases

The risk phrases R36, R37 and R38 can be combined when substances are irritants by more than one route. This results in the following combined risk phrases:

R36/37 *Irritant to eyes and respiratory system*

R36/37/38 *Irritant to eyes, respiratory system and skin*

R36/38 *Irritant to eyes and skin*

R37/38 *Irritant to respiratory system and skin*

The purpose of these risk phrases is to reduce the quantity of information required on the labels needed for the CHIP3 Regulations: they mean that a substance possesses each of the individual risk phrases. For example a classification of R36/37/38 is equivalent to R36, R37 and R38.

C4.4 Limiting Concentrations

"Corrosive" and "Irritant" have specified concentration limits set out in the HWR, above which a waste would be hazardous:

- one or more corrosive substances classified as R35 at a total concentration $\geq 1\%$;
- one or more corrosive substances classified as R34 at a total concentration $\geq 5\%$;
- one or more irritant substances classified as R41 at a total concentration $\geq 10\%$; or
- one or more irritant substances classified as R36, R37, R38 at a total concentration $\geq 20\%$.

C4.5 Procedure for Assessment of Hazards H4 and H8

First, determine whether the waste contains any substances classified with the risk phrases R34, R35, R36, R37, R38, R41 or the related combined risk phrases. If it does, and the concentrations within the waste equal or exceed the relevant thresholds, the waste will be hazardous.

If the waste comprises a complex mixture of substances whose composition is not determined, there are two options:

- use pH to determine if the waste is hazardous and thus avoid testing; or
- use an appropriate test method to determine the corrosivity or irritancy of the waste.

Using pH

If the waste is believed to contain "*dangerous substances*" with a high or low pH and can be leached to produce a leachate that has a pH of 2 or less or a pH of 11.5 or greater it should be assumed to be corrosive and thus be hazardous waste by H8. If pH is being used as the basis of the classification, the acid/alkali reserve⁷ can be taken into consideration. The acid/alkali reserve provides a measure of the capability of an acid or alkali to maintain its pH and combined with pH provides a good indication of corrosivity. If the acid/alkali reserve suggests that a waste may not be corrosive, this must be confirmed by further testing. If the pH is within the range 2 to 11.5 the waste is not corrosive on the basis of pH; but it may still be irritant (see Section C4.6) or corrosive if the presence of, for example, organic hydroperoxides is suspected.

⁷ Young, J.R., How, M.J., Walker, A.P. and Worth, W.H.M. 1988. "Classification as corrosive or irritant to skin of preparations containing acidic or alkaline substances, without testing on animals", *Toxic In Vitro* 2(1): 19-26.

Using testing

Testing should be limited to cases where the hazards cannot be determined from the composition of the waste (i.e. using risk phrases) or by using pH (see above). However, some of the Annex V Test Methods B4 and B5, which correspond best to hazard H4 and H8, rely on animal testing and should not be performed. Details of the approved test methods for hazards H4 and H8 can be found in Section C4.8.

C4.6 Assignment of Appropriate Hazard

After determining whether a waste is hazardous waste, the appropriate hazard should be assigned to the waste so that it can be correctly identified for Duty of Care purposes. The hazards irritant and corrosive are linked because they both refer to the potential for harm or damage to tissue. Corrosive substances exhibit irritant properties at low concentrations.

Threshold concentrations (listed in Article 2 of EWC 2002 for R34 or R35 substances) are the concentrations at which the presence of such substances in a waste would classify it as hazardous. However, at these concentrations the appropriate hazardous property would be H4 (Irritant). Table C4.1 shows the thresholds at which wastes become hazardous (H4 or H8) and the limits for assigning the appropriate hazard.

Regardless of the hazard assigned, wastes with a total concentration of substances classified R35 greater than or equal to 1%, or a total concentration of substances classified R34 greater than or equal to 5%, will be hazardous wastes.

Table C4.1: Limits for Assigning Hazards to Irritant and Corrosive

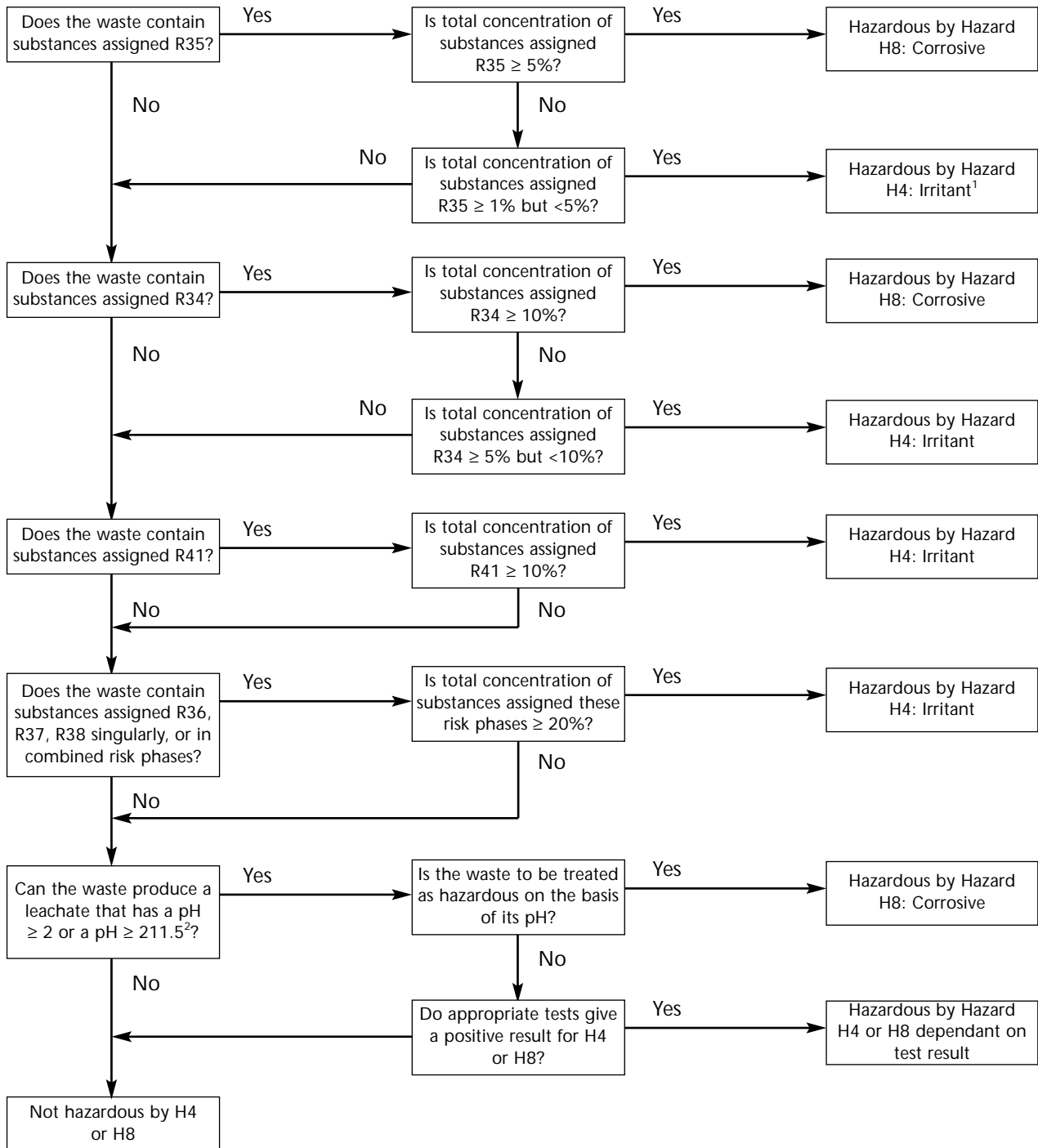
| Risk Phrases | Thresholds for classification as hazardous waste | Limits for assigning hazard | |
|---|--|-----------------------------|---------------|
| | | H4: Irritant | H8: Corrosive |
| Total concentration of substances classified as R35 | ≥ 1% | 1% ≤ total conc. <5% | conc. ≥5% |
| Total concentration of substances classified as R34 | ≥ 5% | 5% ≤ total conc. <10% | conc. ≥ 10% |
| Total concentration of substances classified as R41 | ≥ 10% | conc. ≥ 10% | n/a |
| Total concentration of any substances classified as R36, R37 or R38 | ≥ 20% | conc. ≥ 20% | n/a |

n/a not applicable

C4.7 Decision Tree

Figure C4.1 sets out the assessment process for Hazards H4 and H8.

Figure C4.1: Decision Tree for the Assessment of Hazards H4 and H8



Notes

¹ If the waste also contains substances assigned R34 and the total concentration of those substances is $\geq 10\%$, the waste is hazardous by hazard H8: Corrosive.

² Including consideration of acid/alkali reserve, if appropriate.

C4.8 Test Methods

The test methods which correspond best to the definitions of the hazards H4 and H8 are set out in Table C4.2. The test methods B4 and B5 provided by EC Directive 92/69/EEC for the hazards are not appropriate: as they rely on animal testing and therefore are not considered further.

Table C4.2: Test Methods for Hazards H4 and H8

| Hazard(s) | Test Method | Reference | Acceptability |
|-----------|--|-------------------------|---------------|
| H4 and H8 | B4: Acute toxicity (skin irritation) | EC Directive 92/69/EEC | 1 |
| H4 and H8 | B5: Acute toxicity (eye irritation) | EC Directive 92/69/EEC | 1 |
| H8 | B40: Skin Corrosion (in vitro) Rat Skin TER Assay Human Skin Model Assay | EC Directive 2000/32/EC | 1 ✓ |
| H4 and H8 | pH, including the acid/alkali reserve ⁸ | | ✓ |
| H4 | Neutral Red Assay | Babich H and | ✓ |
| H4 | Neutral Red Release | Borenfreund E (1990) | ✓ |
| H8 | Dermal Biobarrier | In Vitro International | ✓ |

Note:

¹ The Agencies do not endorse destructive animal testing. Their view is that wherever there is any doubt about the corrosive/irritant nature of a waste, the precautionary principle should apply.

The pH is a basic physico-chemical property which assists in establishing whether a waste exhibits H4 or H8 hazards. While pH can be a direct and immediate measurement from liquid waste, assessment of solid waste requires leaching and testing of the leachate. A summary of the draft CEN leaching test and references to other established leaching tests are given in Table C4.3.

Several cytotoxicity tests and biochemical methods give a reasonable correlation with *in vivo* methods for hazards H4 and H8. Other tests are at an early stage of validation and considerable work remains to be done before they can be recommended as alternatives.

⁸ Young, J.R., How, M.J., Walker, A.P. and Worth, W.H.M. 1988. "Classification as corrosive or irritant to skin of preparations containing acidic or alkaline substances, without testing on animals", *Toxic In Vitro* 2(1): 19-26.

Table C4.3: Some Leaching Tests for Solid Materials

| Source | Title | Reference |
|--------------------|--|--|
| CEN | Characterisation of waste – Leaching | <ul style="list-style-type: none"> • BS EN 12457-1: 2002 • BS EN 12457-2: 2002 • BS EN 12457-3: 2002 • BS EN 12457-4: 2002 |
| DIN | Standard Methods for the Examination of Water, Wastewater and Sludge. Sludges and sediments (Group 5). Determination of leachability by water. | DIN 38414 part 4 October 1984 |
| NRA | Leaching Tests for Assessment of Contaminated Land Interim NRA Guidance | NRA R&D Note 301, 1994 |
| NEN | Leaching characteristics of building materials and solid waste material. Leaching tests. Determination of the leaching of inorganic constituents from powder and granular building materials and waste materials | NEN 7343, 1992 |
| AEA | Review of leaching test protocols with a view to developing an accelerated anaerobic leaching test | S.M. Wallis, P.E. Scott and S. Waring. Environment Safety Centre. AEA-EE-0392. 1992 |
| Environment Canada | Compendium of waste leaching test | Environment Canada, 1990. Environmental Protection series. Report EPS 3/HA/7 |
| AFNOR | Waste, Leaching of waste | AFNOR x-31-210. 1992 |

C4.8.1 CEN Leaching Test

The European/UK Standard is designed to be used as a compliance test to provide information on the leaching behaviour of key constituents from granular waste materials and sludges. The test procedure produces eluates, which can subsequently be characterised physically and chemically according to existing standards methods.

The procedures in the Standard are not applicable to monolithic wastes with a cross-section larger than 40 mm (e.g. solidified, encapsulated and vitrified waste). Leaching from monolithic materials is addressed in a separate standard to be developed by CEN.

Special care must be taken when testing waste materials that are not thermodynamically stable under ambient conditions (e.g. materials with reducing or oxidising properties).

Four test procedures are presented in the standard based on different liquid to solid (L/S) ratios because this parameter among others plays an important role in the leaching process. The choice of procedure depends on the degree and type of information needed for compliance.

The sample material, reduced to a particle size of less than 4 mm diameter, is brought into contact with demineralised water under defined conditions according to one of the procedures selected. The standard is based on the assumption that equilibrium or near equilibrium is achieved between the liquid and solid phases during the test period. The solid residue is separated by filtration. The properties of the eluate(s) are measured using methods developed for water analysis and adapted to meet criteria for analysis of eluates.

After the test the leaching conditions in terms of pH, conductivity and redox potential dictated by the waste are recorded: these parameters are important in the interpretation of data since they largely control the leaching behaviour of wastes.

The standard should be referred to for the full experimental procedures covering apparatus, sampling and sample preparation, test conditions and data handling.

C4.8.2 pH Measurement for Hazards H4 and H8

EC Annex V test methods for hazards H4 and H8 specify that further testing need not be carried out if the pH value of the waste is less than 2 or greater than 11.5. If the pH exceeds these limits then the waste should be regarded as hazardous by hazard H8.

When the pH indicates the waste is hazardous, but specific information to indicate whether the waste is hazardous by hazard H4 or H8 is not available, the assessors should assume the waste is corrosive and assign the waste hazard H8. pH measurements can be successfully carried out on moist solid waste and a pH test carried out on a dry solid moistened with a little water can give an indication of a pH which exceeds the above stated limits. Where pH measurements cannot be successfully carried out on solid wastes, an appropriate leaching test should be selected and a determination on the leachate carried out.

If pH is being used as the basis of the classification, the acid/alkali reserve⁹ can be taken into consideration. The acid/alkali reserve provides a measure of the capability of an acid or alkali to maintain its pH, combined with pH it provides a good indication of corrosivity.

The acid/alkali reserve is determined by titration and is expressed as the grams of sodium hydroxide (equivalent) per 100 g of substance required to adjust the pH to the appropriate value. A waste should be considered as corrosive if:

- $\text{pH} + 1/12 \text{ alkali reserve} \geq 14.5$; or
- $\text{pH} - 1/12 \text{ acid reserve} \leq -0.5$.

If a waste is not classified as corrosive on this basis, it may be classified as irritant if

- $\text{pH} + 1/6 \text{ alkali reserve} \geq 13$; or
- $\text{pH} - 1/6 \text{ acid reserve} \leq 1$.

C4.8.3 Neutral Red Uptake Assay for Hazard H4

The neutral red assay detects irritant effects of complex mixtures. This is a simple and fairly rapid test with an objective endpoint. It may be used in micro-titre systems, which are valuable because they utilise very little space, increase the number of replicates and are usually easily automated. This results in a substantial saving in time and manpower.

The method of measuring inhibition of cell growth utilises the uptake of certain dyes, known as vital dyes, by living cells. The method was developed primarily by Babich and Borenfreund (1990)¹⁰ and is based on the uptake of neutral red which is thought to enter living cells by non-ionic diffusion and then accumulates in lysosomes. The dye is excluded from dead cells.

The cells are grown in tissue culture flasks until nearly confluent, harvested and aliquots grown in 24-well micro-titre or tissue culture plates for 24 hours, after which the test solution is removed and inhibition of cell growth measured. As sensitivity is a significant factor when testing complex mixtures the exposure time may be increased to 72 hours.

⁹ Young, J.R., How, M.J., Walker, A.P. and Worth, W.H.M. 1988. "Classification as corrosive or irritant to skin of preparations containing acidic or alkaline substances, without testing on animals", *Toxic In Vitro* 2(1): 19-26.

¹⁰ Babich, H. and Borenfreund, E. 1990. "Applications of the Neutral Red Cytotoxicity Assay to in vitro toxicology", *Alternatives to Animal Experiments*, No 18.

C4.8.4 EC Test Method B40 (Skin Corrosion) for Hazard H8

Introduction

Test Method B40 contains two *in vitro* tests for skin corrosivity:

- a rat skin transcutaneous electrical resistance (TER) assay; and
- a test employing a human skin model.

The Rat Skin TER Assay involves destructive animal testing and is therefore not appropriate.

The human skin model assay enables the correct distinction between degrees of corrosive effect (i.e. severe skin corrosives (R35) and other skin corrosives (R34)).

Principle of the Test Method - Human Skin Model Assay

The test material is applied topically for up to 4 hours to a three-dimensional human skin model, comprising a reconstructed epidermis with a functional stratum corneum. Corrosive materials are identified by their ability to produce a decrease in cell viability (as determined, for example, by using the MTT reduction assay) below defined threshold levels at specified exposure periods. The principle of the assay is in accordance with the hypothesis that chemicals which are corrosive are those which are able to penetrate the stratum corneum (by diffusion or erosion) and are sufficiently cytotoxic to cause cell death in the underlying cell layers.

C4.8.5 Neutral Red Release Test for Hazard H4

An alternative method for irritancy testing, also recommended for use, is a recent modification to the neutral red uptake method – the neutral red release method. This method is based on the release of dye (neutral red) from pre-loaded cells exposed to irritant compounds. The test uses a similar technique to the neutral red uptake test but has been claimed to be more reliable than uptake techniques. Tests in the USA looked at 12 *in vitro* methods: the cytological test “neutral red release” gave the best correlation to standard Draize irritancy tests on rabbits.

C4.8.6 Dermal Biobarrier Test for Hazard H8

A test to determine corrosivity has been developed consisting of two compartments:

- a dermal biobarrier of target macromolecules;
- a chemical detection system (CDS).

The test kit is available ready formulated from In Vitro International.

The biobarrier is prepared by coating a support with a mixture of diluent and solubilised proteins. The macromolecules are gelled onto a cellulose support within a circular disc deliverable system. The biobarrier is then sealed and stored at 4°C. The CDS consists of multiple chemical detectors.

Test substances either solid or liquid are applied directly to the dermal biobarrier. When the chemical destroys the biobarrier it is detected by the CDS which produces a simple colour change. The colour change is detected by eye and the amount of time for the colour change to occur is related to the corrosivity of the substances. If no colour change occurs then the substance is non-corrosive.

This test has produced reliable results in validation exercises with *in vitro* effects and also reproducibility tests. It should also be remembered that pH testing is also appropriate for the identification of this hazard.

Appendix C:

C5 Assessment of Hazards H5/H6: Harmful and Toxic

C5.1 Definition

"Harmful" (H5) and "Toxic" (H6) hazards are linked.

Annex III of the HWD defines H5 "Harmful" as:

"substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risks".

Annex III of the HWD defines H6 "Toxic" as:

"substances and preparations (including very toxic substances and preparations) which, if they are inhaled or ingested or if they penetrate the skin, may involve serious, acute or chronic health risks and even death".

C5.2 Risk Phrases

The risk phrases associated with the hazards harmful and toxic are:

R20 *Harmful by inhalation*

This risk phrase is assigned to substances and preparations if the results of acute toxicity tests are:

- LC₅₀ inhalation, rat for aerosols or particulates: $1 < LC_{50} \leq 5 \text{ mg/litre/4 hours}$; or
- LC₅₀ inhalation, rat for gases or vapours: $2 < LC_{50} \leq 20 \text{ mg/litre/4 hours}$.

R21 *Harmful in contact with skin*

This risk phrase is assigned to substances and preparations if the results of acute toxicity tests are:

- LD₅₀ dermal, rat or rabbit: $400 < LD_{50} \leq 2,000 \text{ mg/kg}$.

R22 *Harmful if swallowed*

This risk phrase is assigned to substances and preparations if the results of acute toxicity tests are:

- LD₅₀ oral, rat: $200 < LD_{50} \leq 2,000 \text{ mg/kg}$; or
- discriminating dose, oral, rat, 50 mg/kg: 100% survival but evident toxicity, or
- less than 100% survival at 500 mg/kg oral, rat by the fixed dose procedure; or
- high mortality in the dose range > 200 to $\leq 2,000 \text{ mg/kg}$ oral, rat, by the acute toxic class method.

R23 *Toxic by inhalation*

This risk phrase is assigned to substances and preparations if the results of acute toxicity tests are:

- LC₅₀ inhalation, rat for aerosols or particulates: $0.25 < LC_{50} \leq 1 \text{ mg/litre/4 hours}$; or
- LC₅₀ inhalation, rat for gases or vapours: $0.5 < LC_{50} \leq 2 \text{ mg/litre/4 hours}$.

R24 *Toxic in contact with skin*

This risk phrase is assigned to substances and preparations if the results of acute toxicity tests are:

- LD₅₀ dermal, rat or rabbit: 50 < LD₅₀ ≤ 400 mg/kg.

R25 *Toxic if swallowed*

This risk phrase is assigned to substances and preparations if the results of acute toxicity tests are:

- LD₅₀ oral, rat: 25 < LD₅₀ ≤ 200 mg/kg, or
- discriminating dose, oral, rat, 5 mg/kg: 100% survival but evident toxicity; or
- high mortality in the dose range > 25 to ≤ 200 mg/kg oral, rat, by the acute toxic class method.

R26 *Very toxic by inhalation*

This risk phrase is assigned to substances and preparations if the results of acute toxicity tests are:

- LC₅₀ inhalation, rat for aerosols or particulates: ≤ 0.25 mg/litre/4 hours, or
- LC₅₀ inhalation, rat for gases or vapours: ≤ 0.5 mg/litre/4 hours.

R27 *Very toxic in contact with skin*

This risk phrase is assigned to substances and preparations if the results of acute toxicity tests are:

- LD₅₀ dermal, rat or rabbit: ≤ 50 mg/kg.

R28 *Very toxic if swallowed*

This risk phrase is assigned to substances and preparations if the results of acute toxicity tests are:

- LD₅₀ oral, rat: ≤ 25 mg/kg; or
- less than 100% survival at 5 mg/kg oral, rat by the fixed dose procedure; or
- high mortality in the dose range ≤ 25 mg/kg oral, rat, by the acute toxic class method.

R39 *Danger of very serious irreversible effects*

This risk phrase is assigned if there is strong evidence that irreversible damage is likely to be caused by a single exposure by an appropriate route. In order to indicate the route, R39 is combined with R23 to R28 or the combined risk phrases detailed below (Section C5.3) related to toxic and very toxic. The doses related to the single exposure are those related to the risk phrases R23 to R28 detailed above.

R48 *Danger of serious damage to health by prolonged exposure*

This risk phrase is assigned if serious damage is likely to be caused by repeated or prolonged exposure by an appropriate route. It is only associated with toxic and harmful and is combined with R20 to R25 or the combined risk phrases, related to R20 to R25, detailed below related to toxic and harmful, to indicate the route. However, the doses are as follows:

"Toxic with R48"

- oral, rat: ≤ 5 mg/kg (bodyweight)/day
- dermal, rat or rabbit: ≤ 10 mg/kg (bodyweight)/day
- inhalation, rat: ≤ 0.025 mg/litre, 6 hrs/day

"Harmful with R48"

- oral, rat: ≤ 50 mg/kg (bodyweight)/day
- dermal, rat or rabbit: ≤ 100 mg/kg (bodyweight)/day
- inhalation, rat: ≤ 0.25 mg/litre, 6 hrs/day.

R65 *Harmful, may cause lung damage if swallowed*

This risk phrase is assigned to liquid substances and preparations presenting an aspiration hazard in humans because of their low viscosity.

R68 *Possible risk of irreversible effects*

This risk phrase is assigned if there is strong evidence that irreversible damage is likely to be caused by a single exposure by an appropriate route. In order to indicate the route, R68 is combined with R20 to R22 or the combined risk phrases detailed below related to harmful. The dose related to the single exposure are those related to the risk phrases R20 to R22.

C5.3 Combined Risk Phrases

The above risk phrases can be combined when a substance is harmful, toxic or very toxic by more than one route. This results in the following combined risk phrases:

R20/21 *Harmful by inhalation and in contact with skin*

R20/21/22 *Harmful by inhalation, in contact with skin and if swallowed*

R20/22 *Harmful by inhalation and if swallowed*

R21/22 *Harmful in contact with skin and if swallowed*

R23/24 *Toxic by inhalation and in contact with skin*

R23/24/25 *Toxic by inhalation, in contact with skin and if swallowed*

R23/25 *Toxic by inhalation and if swallowed*

R24/25 *Toxic in contact with skin and if swallowed*

R26/27 *Very toxic by inhalation and in contact with skin*

R26/27/28 *Very toxic by inhalation, in contact with skin and if swallowed*

R26/28 *Very toxic by inhalation and if swallowed*

R27/28 *Very toxic in contact with skin and if swallowed*

In addition, these risk phrases can be combined with R39, R48 and R68 (when used with a substance classified as Xn Harmful) in order to identify the appropriate routes and risks of exposure.

The purpose of these combined risk phrases is to reduce the quantity of information required on the labels needed for the CHIP Regulations. They mean that a substance possesses each of the individual risk phrases.

C5.4 Limiting Concentrations

"Harmful" and "Toxic" have specified concentration limits set out in the HWD, above which a waste would be hazardous:

- one or more substances classified as very toxic at a total concentration $\geq 0.1\%$;
- one or more substances classified as toxic at a total concentration $\geq 3\%$; or
- one or more substances classified as harmful at a total concentration $\geq 25\%$.

C5.5 Procedure for Assessment of Hazards H5 and H6

First, determine whether the waste contains any substances classified with the risk phrases R20 to R28, R39, R48, Xn R68 or the combined risk phrases. If it does and the concentrations within the waste equal or exceed the relevant thresholds the waste will be hazardous.

It must be remembered that:

- the concentrations of very toxic substances can only be added to the concentrations of other very toxic substances;

- the concentrations of toxic substances can only be added to the concentrations of other toxic substances;
- the concentrations of harmful substances can only be added to the concentrations of other harmful substances.

This means that the concentrations of very toxic substances cannot be added to the concentrations of toxic or harmful substances. Toxic substances cannot be added to the concentrations of very toxic or harmful substances. Harmful substances cannot be added to very toxic or toxic substances.

For R65, the classification is harmful and therefore the concentrations of R65 substances can be added to the concentrations other harmful substances.

R68 substances can only be considered for H5 if the substance is classified as harmful. If a substance is classified as Mutagenic Category 3; R68 it should be assessed under Hazard H11 "mutagenic" (see Appendix C11). Substances classified as Mutagenic Category 3; R68 have a much lower threshold limit than substances classified Harmful; R68 (1% compared to 25%).

C5.6 Assignment of Appropriate Hazard

After determining whether a waste is hazardous waste, the appropriate hazard should be assigned to the waste so that it can be correctly identified on the consignment note. As stated in Section C5.1, there is a link between the hazards harmful, toxic and very toxic, with toxic or very toxic substances exhibiting harmful properties at low concentration.

The threshold values given in Article 2 of EWC 2002, for toxic and very toxic substances, are the concentrations at which the presence of such substances in a waste would classify it as hazardous. However, at these concentrations the appropriate hazard for a waste would be H5 (Harmful). Only at higher concentrations will the substances classified as toxic or very toxic be assigned the hazard H6 (Toxic). Table C5.2 shows the thresholds at which wastes become hazardous (by H5 or H6) and limits for assigning the appropriate hazard. This follows from the CHIP3 Regulations.

Regardless of the hazard assigned, wastes will be hazardous if:

- the total concentration of substances classified as very toxic is equal to or greater than 0.1%; or
- the total concentration of substances classified as toxic is equal to or greater than 3%; or
- the total concentration of substances classified as harmful is equal to or greater than 25%.

Table C5.1: Limits for Assigning Hazards to Harmful and Toxic

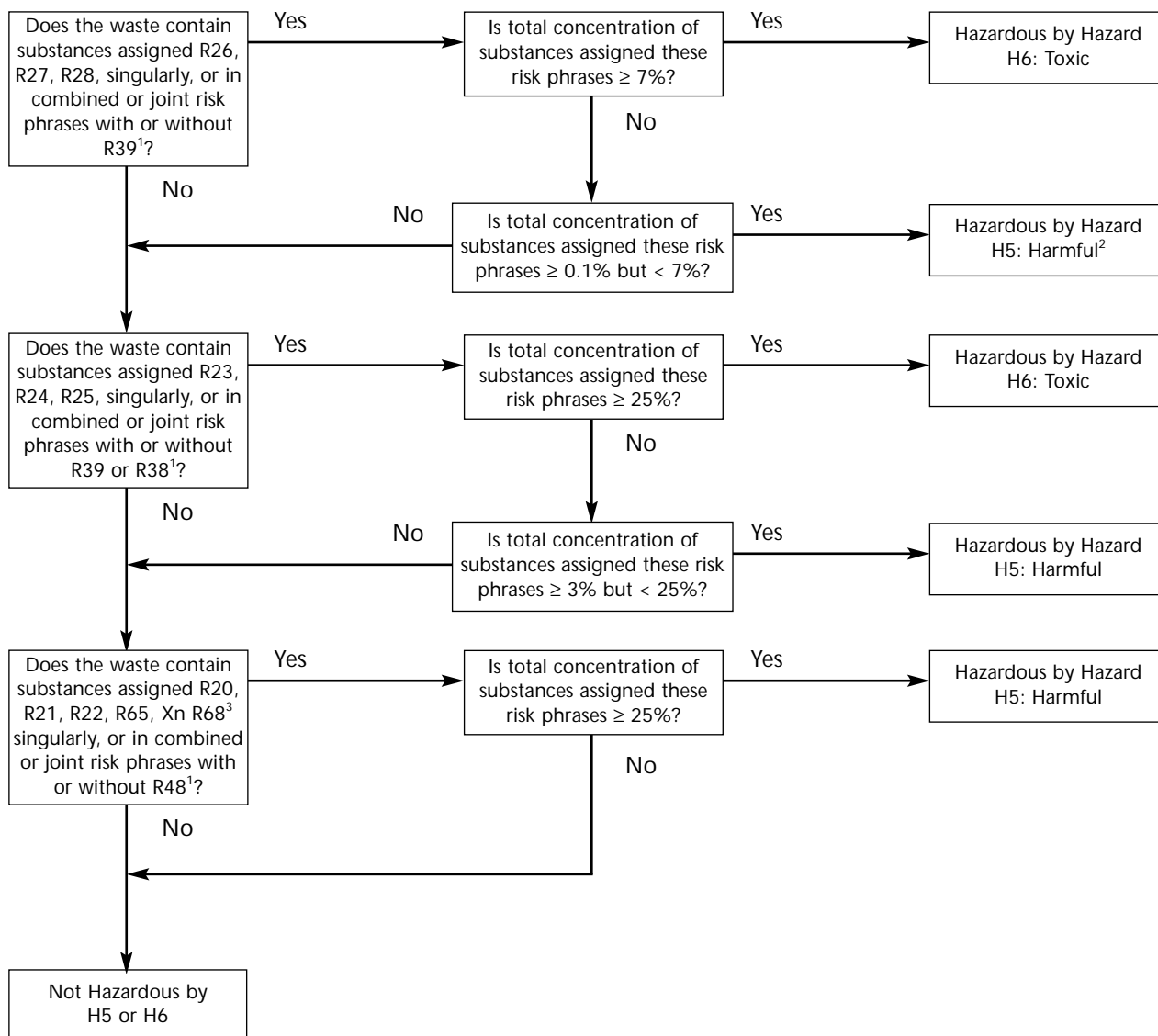
| Classification | Risk Phrases | Thresholds for classification as hazardous waste | Limits for assigning hazard | |
|----------------|--|--|-----------------------------|-----------|
| | | | H5: Harmful | H6: Toxic |
| Very Toxic | R26, R27, R28, and combined risk phrases with or without R39 | ≥ 0.1% | 0.1% ≤ total conc. < 7% | ≥ 7% |
| Toxic | R23, R24, R25, and combined risk phrases with or without R39 or R48 | ≥ 3% | 3% ≤ total conc. < 25% | ≥ 25% |
| Harmful | R20, R21, R22, R65, Xn R68 and combined risk phrases with or without R48 | ≥ 25% | ≥ 25% | n/a |

n/a not applicable

C5.7 Decision Tree

Figure C5.1 sets out the assessment process for the Hazards H5 and H6.

Figure C5.1: Decision Tree for the Assessment of Hazards H5 and H6



Notes

¹ There are no substances with the classification R39 or R48 alone. In order to indicate the route these are combined with R20 to R28 or the combined risk phrases.

² If the waste also contains substances classified as toxic and the total concentration of those substances is ≥ 25%, the waste is hazardous by Hazard H6: Toxic.

³ R68 can only be considered for H5 if the substance is classified Xn harmful. If a substance is classified as Mutagenic Category 3, it must be assessed under H11. In order to indicate the route R68 can be combined with R20 to R22 or the combined risk phrases relating to harmful.

C5.8 Test Methods

The test methods which correspond best to the definitions of the hazards H4 and H8 are set out in Table C5.2.

Table C5.2: Test methods for hazards H5 and H6

| Hazard | Test Method | Source | Acceptability |
|----------------|-----------------------------------|------------------------------|----------------|
| H5 and H6 | B1 | EC Directive 92/69/EEC | 1 |
| H5 and H6 | B1.bis | EC Directive 92/69/EEC | 1 |
| H5 and H6 | B1.trs | EC Directive 96/54/EC | 1 |
| H5 and H6 | B2 | EC Directive 92/69/EEC | 1 |
| H5 and H6 | B3 | EC Directive 92/69/EEC | 1 |
| H6 | B7 | EC Directive 92/69/EEC | 1 |
| H6 | B8 | EC Directive 92/69/EEC | 1 |
| H6 | B9 | EC Directive 92/69/EEC | 1 |
| H5 and H6 | B26 | EC Directive 2000/59/EC | 1 |
| H5 and H6 | B27 | EC Directive 2000/59/EC | 1 |
| H5, H6 and H14 | Bacterial bio-luminescence assay | Liu, D. and Dutke, B.J. 1984 | ✓ ² |
| H5, H6 and H14 | Enhanced chemi-luminescence assay | Hayes, E. and Smith, M. 1996 | ✓ ² |

Notes:

¹ The Agencies do not endorse destructive animal testing. Wherever there is any doubt about the toxicity of a waste, the precautionary principle should apply.

² While these are predominantly applicable to H14, they will also serve as indicators for H5 and H6.

None of the EC Annex V tests is approved by the Agencies for use, because of their reliance on animal testing.

There are many alternative toxicity tests available but it is important to select those that are suitable for assessing the toxicity of complex substances. Two commercially available screening tests can be used to identify hazards H5 and H6 (and is also applicable to H14, see Appendix C14) in a wide range of substances. These are:

- the bacterial bioluminescence assay test;
- the enhanced chemiluminescence assay test.

These tests are well established, but do not differentiate between toxicity (to man) and ecotoxicity. There are no appropriate rapid screening tests available that are solely hazard H5 and/or H6 specific.

C5.9 Screening Tests for Hazards H5 and H6

C5.9.1 Bacterial Bioluminescence Assay Test

These assays using *Vibrio fischeri* (formerly known as *Phyrobacterium phosphoreum*) have been validated specifically for assessing toxicity of hazardous wastes and show good correlation with higher organisms (Bulich, A.A. in Liu and Dutke 1984).¹¹ The use of freeze dried or lyophilised bacteria allows tests to be conducted without extensive preparation or pre-planning. The test is available as a standardised commercial package from the Microbics Corporation.

The test is simple and rapid, and provides an indication of toxicity after a 5–30 minute exposure period. The test measures light output from the bioluminescent bacterium which is inhibited in the presence of pollutants. This is in contrast to other acute toxicity tests of comparable sensitivity, which typically requires exposure periods of between 24 and 96 hours. The constant test capability can therefore be achieved with minimum laboratory space.

The *Vibrio fischeri* bioluminescence test is generally less sensitive to aquatic contaminants than higher organism tests. Low level toxicity, which may render a waste hazardous, may not always be detected by bacterial bioluminescence.

The test is sensitive to the toxicity of sewage effluents, petroleum effluents and industrial effluents but not those containing high levels of urea, cyanide or ammonia. Bioluminescence in *Vibrio fischeri* is not as sensitive as other acute tests to insecticides, herbicides, textile effluents, highly lipophilic contaminants or to wastes with a high inorganic content.

Procedures for using *Vibrio fischeri* bioluminescence assays are detailed in the manuals published by the Microbics Corporation. The Environment Agency's SCA (Standing Committee of Analysts) "Blue Book" contains a method for acute toxicity to bioluminescent bacteria. The test is also recognised by ASTM, DIN and other bodies.

C5.9.2 Enhanced Chemiluminescent Assay Test

These assays involve a free radical reaction based upon the oxidation of luminol in the presence of the enzyme horseradish peroxidase. Horseradish peroxidase is used as the conjugate because of its stability and commercial availability. The reaction emits light at a relatively constant rate. If free radical scavengers such as anti-oxidants are added to the reaction, light emission is stopped or delayed. Any substance capable of inhibiting the enzyme will also cause a reduction, or complete inhibition of light output.

The technique is commercially available and full guidance¹² on the methodology is provided in the form of user manuals with the required hardware and reagents from the manufacturers.

¹¹ Liu, D. and Dutke, B.J. 1984. Toxicity Screening Procedures Using Bacterial Systems. Marcel Dekker Inc.

¹² Hayes, E. and Smith, M. 1996 "Eclox: A Rapid Screening Toxicity Test." Toxic Impacts of Waste on the Aquatic Environment, Tapp, J.F. et al. (Eds) Royal Society of Chemistry, pp. 94-103.

Appendix C:

C6 Assessment of Hazard H6: Toxic

Assessment of Hazard H6, Toxic, is carried out alongside the assessment of Hazard H5, Harmful, in Appendix C5.

Appendix C:

C7 Assessment of Hazard H7: Carcinogenic

C7.1 Definition

Annex III of the HWD defines H7 "Carcinogenic" as:

"substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence".

C7.2 Risk Phrases

For the purposes of classification and labelling, carcinogens are divided into three categories:

Category 1:

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

Category 2:

Substances which should be regarded as if they are carcinogenic to man. There is sufficient evidence to provide a strong presumption that human exposure to a substance may result in the development of cancer, generally on the basis of:

- (a) appropriate long-term animal studies*
- (b) other relevant information.*

Category 3:

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

The following risk phrases apply:

Categories 1 and 2:

- R45 *May cause cancer*
- R49 *May cause cancer by inhalation*

Category 3:

- R40 *Limited evidence of a carcinogenic effect*

C7.3 Limiting Concentration

"Carcinogenic" has specified concentration limits set out in the HWR, above which a waste would be hazardous:

- one substance known to be carcinogenic of category 1 or 2 at a concentration $\geq 0.1\%$; and
- one substance known to be carcinogenic of category 3 at a concentration $\geq 1\%$.

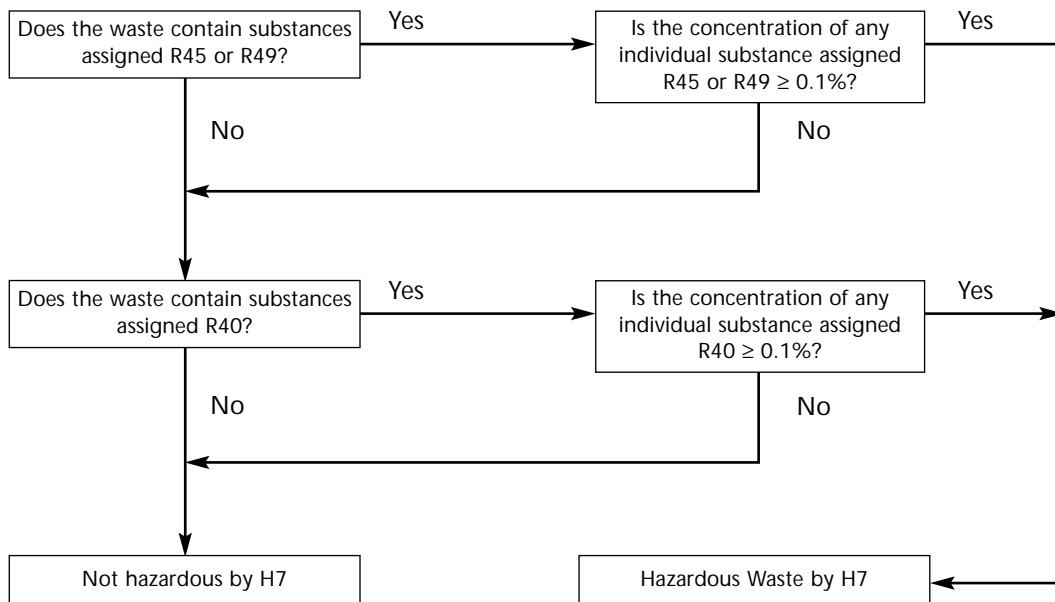
Wastes containing category 1 or 2 carcinogens (i.e. substances with risk phrases R45 or R49) will be hazardous if the concentration of any one of those substances is $\geq 0.1\%$ w/w in the waste. It should be noted that this is a change from the classification under the Special Waste Regulations 1996, under which the concentrations of category 1 and 2 carcinogens were additive. The new criterion means that an individual category 1 or 2 carcinogen must be present at a concentration $\geq 0.1\%$.

Wastes containing category 3 carcinogens (i.e. substances with risk phrases R40) will be hazardous if the concentration of any one of those carcinogens is $\geq 1\%$ w/w in the waste. This is a change from classification under the Special Waste Regulations 1996, as category 3 carcinogens were not included in the assessment criteria.

C7.4 Decision Tree

Figure C7.1 sets out the assessment process for the Hazard H7.

Figure C7.1: Decision Tree for the Assessment of Hazard H7



C7.5 Test Methods

None of the EC test methods published corresponds to the definition of the hazard carcinogenic.

Simple *in vitro* tests are unable to identify those compounds which are carcinogenic. Even utilising *in vivo* tests for carcinogenicity would be unsuitable for the classification of wastes as the testing requires several months to complete. The genotoxicity tests are the only *in vitro* techniques that are enshrined in regulatory toxicology. Detailed guidance is provided on test protocols and interpretation by the UK Environmental Mutagen Society (UKEMS).

Tests are available to give some indication of carcinogenic potential, by studying the mutagenic effects of compounds. However, these tests will not give a definitive result for hazard H7. The recommended non-mammalian tests for H11, mutagenicity, are found in Section C11, and some of these tests (e.g. Test Method B10) can be used to screen for possible mammalian carcinogens.

Appendix C:

C8 Assessment of Hazard H8: Corrosive

Assessment of Hazard H8, Corrosive, is carried out alongside the assessment of Hazard H4, Irritant, in Appendix C4.

Appendix C:

C9 Assessment of Hazard H9: Infectious

C9.1 Definition

Annex III of the HWD defines H9 "Infectious" as:

"substances containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms."

C9.2 Background

Unlike the other hazardous properties there are no absolute criteria for the determination of infectious H9. The CHIP Regulations apply to chemical hazards, so do not include any risk phrases related to the risk of infection.

Clinical judgement is required to determine if a healthcare waste should be considered infectious. This judgement should be based on clinical symptoms and knowledge. It is unlikely that it will be practical or possible to identify specific pathogens within the waste at the point and time of production. The procedure for determining whether a waste is considered hazardous by H9 must therefore assume that the disease causing agent has not been identified.

The definition of H9 includes "micro-organisms or their toxins". This indicates that toxins produced by micro-organisms (e.g. bacteria, fungi, algae) should be assessed for H9 rather than grouped with chemical toxins. The "or" also indicates that H9 should be used even if the producing organism is no longer present. Examples include:

- *Clostridium botulinum* and *C. perfringens*,
- Toxigenic *Vibrio*, *Cholerae* and *Verocytotoxin* or *enterotoxin* producing *E.coli*
- *Cyanobacteria* - blue green algae, *Dinophyceae* - (Paralytic/Diarrhoetic Shellfish Poisoning, Fish Kills)

C9.3 Principle for Assessing Hazard H9

The underlying principle to be considered when assessing H9 is the recognition that many waste streams contain pathogens. However, where there is a low probability that infectious substances are present, where the concentration is at a level naturally encountered, or where the infectious fraction has been removed by specific segregation at source, a waste would not be hazardous by H9.

C9.4 Assessment Procedure

Due to the unique nature of H9, the assessment procedure has been split into two sections:

- waste arising from human or animal healthcare (i.e. those under EWC Chapter 18); and
- potentially infectious wastes from other sources (Chapters 1-17, 19 and 20).

C9.4.1 Chapter 18: Wastes From Human or Animal Healthcare

The key entries under Chapter 18 are:

| | |
|-----------|---|
| 18 01 | wastes from natal care, diagnosis, treatment or prevention of disease in humans |
| 18 01 03* | wastes whose collection and disposal is subject to special requirements in order to prevent infection |
| 18 02 | wastes from research, diagnosis, treatment or prevention of disease involving animals |
| 18 02 02* | wastes whose collection and disposal is subject to special requirements in order to prevent infection |

Both of these entries (18 01 03 and 18 02 02) are absolute entries, without threshold concentrations.

The assessment of H9 for chapter 18 wastes is based on the identification of "*special requirements*". Figure C9.1 provides the assessment method to determine whether a waste is covered by "special requirements" and Table C9.1 provides examples of the application of the assessment methodology.

This assessment for subchapter 18 01 encompasses clinical waste and laboratory waste from human healthcare, which is subject to a range of controls on its collection and disposal aimed at preventing infection. For subchapter 18 02, relating to animal healthcare, the assessment follows the same principles as 18 01. However, no reference is made to clinical waste as its definition is incompatible with pathogens that do not affect humans.

The "infectious" fraction of clinical (or animal healthcare) waste should be identified and segregated on the basis of "*subject to special requirements*". These requirements are in addition to that which is normally required for clinical (or animal healthcare) waste.

"Special requirements" (and H9) apply where the source person or animal is known or clinically assessed to have a disease/infection caused by a micro-organism or its toxin **and** the waste is likely to contain the infectious agent or toxin.

The clinical assessment should be carried out by a healthcare professional who is familiar with the current medical condition and, where feasible, the past medical history of the patient. Where no healthcare worker is involved in the disease diagnosis, special requirements do not apply.

Identification of the pathogen, or classification by other methods, such as the Advisory Committee on Dangerous Pathogens (ACDP) classification groups, is **not** necessary for the purpose of the H9 assessment.

The assessment methodology also recognises that the majority of animal/human healthcare patients will not be suffering from diseases caused by micro-organisms or their toxins. The clinical (or animal healthcare) waste produced from these patients may contain pathogens, but may not be subject to special requirements. Special requirements is assessed on the basis of known infection, whereas, clinical waste is defined on a precautionary basis using the premise that the waste "may cause infection".

Minor ailments (e.g. common cold) are not considered as "subject to special requirements" where they require no healthcare intervention (see example in table C9.1).

Note: Waste Segregation

Clinical (or animal healthcare) wastes subject to special requirements should be specifically segregated from other clinical (or animal healthcare) wastes.

Where clinical (or animal healthcare) wastes arising from animals/humans, which meet the definition of "special requirements", are not specifically segregated from the other clinical wastes, the whole body of the waste should be considered subject to special requirements, infectious, and hazardous by H9.

C9.4.2 Other Sources of Potentially Infectious Waste

Non-healthcare waste streams, where there is a low probability that infectious substances are present, or where the concentration is at a level naturally encountered, should not be classified as hazardous by H9. Examples are foodstuffs, water samples, living persons, and substances which have been treated so that pathogens have been neutralised or deactivated.

The term "natural levels" is difficult to define, but can be taken to accept the presence of pathogens in a **generally healthy** population or environment. This would encompass, for example, sludges arising from waste water treatment and municipal black bag waste.

The interpretation should therefore be based on where it is known or risk assessed that the waste is enriched with the infectious organism or microbial toxin. An example would be where the industrial, or commercial, activity introduces infectious micro-organisms into waste water treatment sludge, or affects the foul waste input so as to increase the numbers of pathogens normally present.

Toxins from micro-organisms act in the same way as toxic chemicals and should be assessed using the threshold criteria outlined for H6. Care should be taken in the use, and source, of toxicity data. It is anticipated that many, if not the majority, of the microbial toxins covered by this hazard will be either "very toxic" or "toxic" and the appropriate thresholds should be used, 0.1% or 3% respectively (e.g. microcystin from cyanobacteria). Where these toxins are present above the threshold concentration the appropriate hazards are H9 and H6.

Figure C9.2 provides the assessment method to determine whether a non-healthcare waste is covered by H9 and Table C9.2 provides examples of the application of the assessment method.

C9.4.3 Organism Classification

The identification of the pathogen, or its classification by hazard group, is not required for the assessments outlined.

There are a number of classification schemes for micro-organisms. These relate primarily to the safety of personnel working with biological agents that are human pathogens. They are not considered relevant to waste classification.

However, where micro-organisms have already been classified, for other purposes, using the Advisory Committee on Dangerous Pathogens system; groups 2, 3 and 4 are considered to cause disease in humans. No equivalent list is available for other living organisms.

C.9.5 Decision Tree

Figures C9.1 and C9.2 set out the assessment process for the Hazard H9.

Figure C9.1: Chapter 18 Wastes – Special Requirements

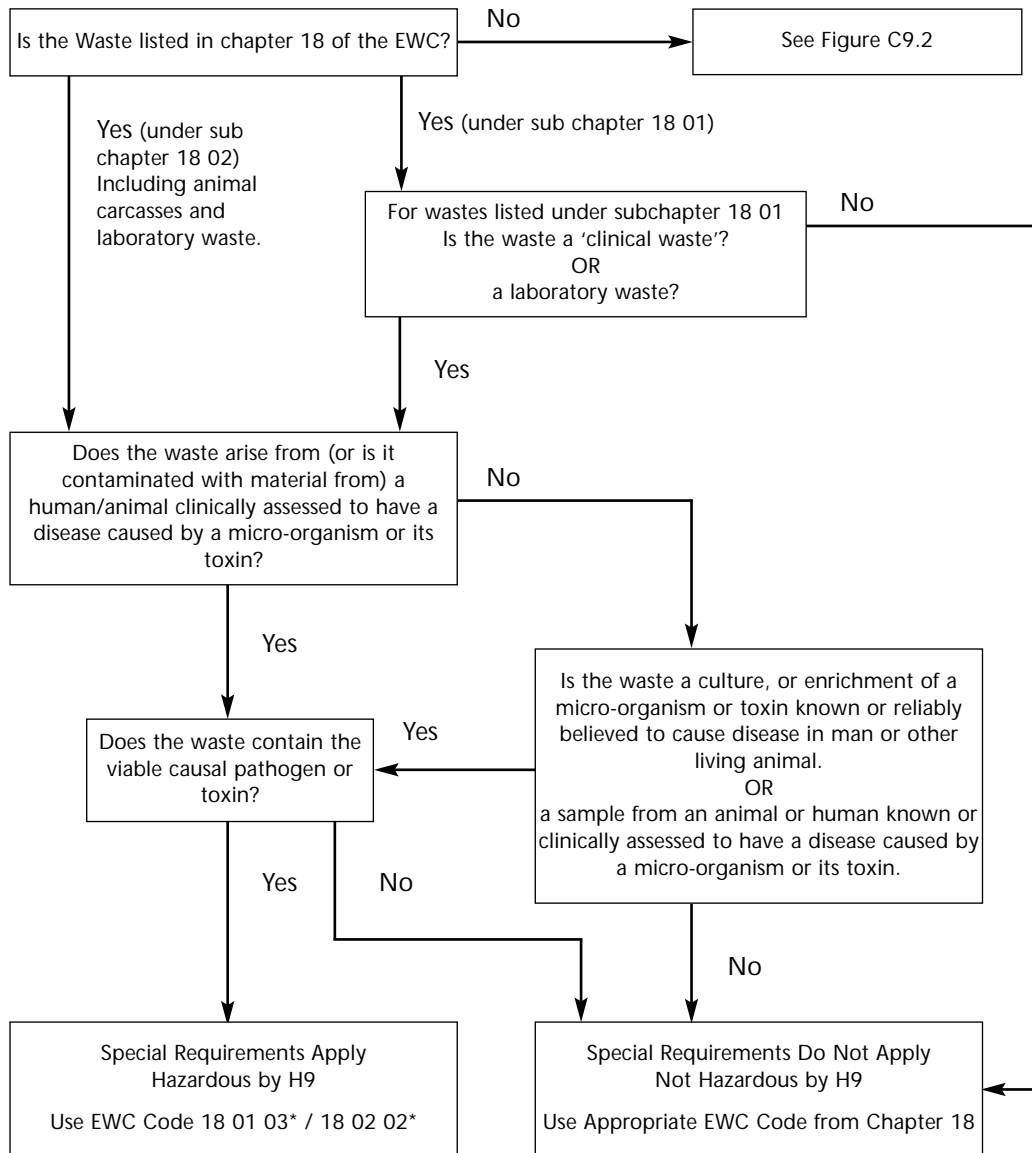
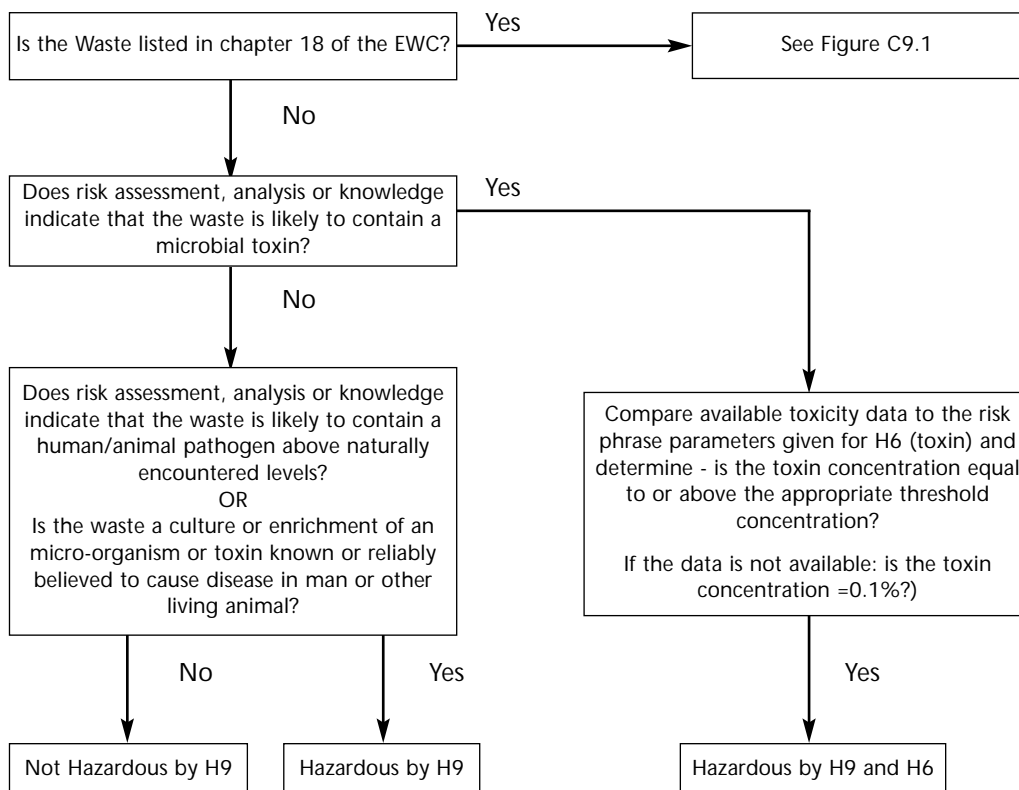


Figure C9.2: Potentially infectious wastes from other sources (Chapters 1-17, 19 and 20)



C9.6 Test Methods

The potential hazards posed by different types of wastes are not fully documented and tests to quantitatively define all hazards associated with wastes do not exist.

Micro-organisms may not be distributed homogeneously throughout a waste stream. Sampling must therefore be representative of, and appropriate to, the waste stream. Additionally, any analysis should only be carried out at a suitably accredited laboratory, using relevant and appropriate analytical methods.

Table C9.1: Examples From Chapter 18 of the EWC – Healthcare Wastes (see Figure C9.1 for assessment procedure)
(Note: This is not an inclusive list)

| Source | Special Requirements Apply (Hazardous by H9) | Special Requirements DO NOT apply |
|---|--|---|
| Hospital, GP surgery veterinary practice nursing home | <i>Clinical (or animal healthcare) waste which has not been subject to specific segregation protocols to remove waste subject to “special requirements”.</i> | Non-clinical waste |
| | The specifically segregated “special requirements” fraction of clinical (or animal healthcare) waste. | Clinical (or animal healthcare) waste where the “special requirements” fraction has been removed by specific segregation. |
| | <p>Clinical (or animal healthcare) waste arising from a patient clinically assessed or known to have a disease caused by a micro-organism or its toxin. Where the causal pathogen or toxin is present in the waste.</p> <ul style="list-style-type: none"> Waste from infectious disease cases. Waste from wound infections (and other hospital acquired infections, e.g. gastrointestinal infections). Waste from patients with microbial diseases that do not relate to the healthcare procedure – e.g. orthopaedic or maternity waste from patients with microbial infections (where the waste contains the causal pathogen) – for example HIV, Hepatitis B, rubella, measles, influenza etc. Waste, containing the pathogen, from a patient with a sore throat (or other minor ailment resulting from a microbial infection) attending a GP’s surgery and receiving healthcare for that ailment. | <p>Clinical (or animal healthcare) waste from patients who are not known, or clinically assessed, to have a disease caused by a micro-organism or its toxin.</p> <ul style="list-style-type: none"> Clinical waste from orthopaedic patients who are unaffected by microbial disease. Clinical waste from patients with certain microbial diseases that do not relate to the healthcare procedure, where these ailments are minor or trivial and have no bearing on the healthcare being provided. For example, a patient receiving orthopaedic care with a common cold, sore throat, or cold sores which are considered minor (because they present negligible threat to the patient or others, do not require treatment or measures to prevent transmission and are likely to be self-resolving). Clinical waste from admissions to Accident and Emergency where knowledge or clinical assessment does not indicate microbial disease. |

Table C9.1: Examples From Chapter 18 of the EWC – Healthcare Wastes (see Figure C9.1 for assessment procedure)
 (Note: This is not an inclusive list)

| Source | Special Requirements Apply (Hazardous by H9) | Special Requirements DO NOT apply |
|---|--|---|
| Community (non medical or veterinary premises) | Human hygiene waste where risk assessment indicates that the waste is clinical because the source has a microbial disease (or animal hygiene waste where special requirements apply) AND clinical diagnosis or assessment has been made. | Human/animal hygiene waste which is non-clinical. Clinical waste (or animal healthcare waste) from people (or animals) who have not been clinically assessed to have a disease caused by a micro-organism or its toxin. |
| | <ul style="list-style-type: none"> • Dog faeces from a boarding kennels with an outbreak of gastrointestinal disease diagnosed by a veterinarian. • Sharps waste from tattooists, ear piercing, or first aid where the source is known to have a microbial disease that is present in the waste. | <ul style="list-style-type: none"> • Drug related litter (note: may be hazardous due to presence of prescription only medicines) • The majority of community sharps waste. • Dog faeces from collection bins • Waste from animal healthcare conducted by the owner/keeper where microbial disease has not been diagnosed by a veterinarian. |
| Laboratory waste (including microbiological waste from colleges, environmental and food analysis) | <p>Cultures of human and animal pathogens, or solutions of their toxins (above threshold concentration)</p> <p>Clinical samples from people or animals known or clinically assessed to have a microbial disease, if the sample contains the causal pathogen or toxin</p> | <p>Cultures of pathogens that are non-pathogenic to man or other organisms</p> <p>Clinical samples from source individuals not known or clinically assessed to have a microbial disease.</p> <ul style="list-style-type: none"> • Blood and urine and stool samples which come from such patients. (Even where samples are likely to contain pathogens in a healthy individual). |
| Pharmaceutical waste | Live vaccines | Most pharmaceuticals – Note this waste may be considered hazardous by assessment procedures elsewhere in this document. |

Table C9.2: Examples From Chapters 1 to 17, 19 and 20 of the EWC – Non-Healthcare Wastes (see Figure C9.2 for assessment procedure)
(Note: This is not an inclusive list)

| Source | Infectious - Hazardous by H9) | Not Hazardous by H9) |
|--|---|----------------------|
| Construction and demolitions wastes | Canal dredgings, or surface skimmings, from a site where a cyanobacterial bloom has occurred AND where risk assessment or analysis indicates a toxin above the appropriate threshold concentration. | |
| Municipal wastes | Where EWC entries permit assessment, AND the assessment procedure in Figure C9.2 indicates. | |

Appendix C:

C10 Assessment of Hazard H10: Toxic for Reproduction

C10.1 Definition

In the HWD the term for H10 is "teratogenic". In Directive 92/32/EEC amending for the seventh time Dangerous Substance Directive 67/548/EEC the term "toxic for reproduction" was introduced and replaced the term "teratogenic". The two definitions are set out below and highlights slight differences between the definitions, with "teratogenic" making no references to effects on fertility.

Annex III of the HWD defines H10 "Teratogenic" as:

"substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce non-hereditary congenital malformations or increase their incidence".

Dangerous Substance Directive defines "Toxic to reproduction" as:

"substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may produce or increase the incidence of non-heritable adverse effects in the progeny and/or of male or female reproductive functions or capacity".

However, the EWC 2002, states that the term "toxic for reproduction" is considered to be in line with hazard H10 in Annex III to Hazardous Waste Directive. Therefore the assessment of Hazard H10 is based on the definition of "toxic for reproduction" and the associated risk phrases, with the term "teratogenic" replaced by term "toxic for reproduction".

C10.2 Risk Phrases

For the purposes of classification and labelling, substances which are "toxic to reproduction" are divided into three categories:

Category 1:

- (a) *Substances known to impair fertility in humans. There is sufficient evidence to establish a causal relationship between human exposure to the substance and impaired fertility.*
- (b) *Substances known to cause developmental toxicity in humans. There is sufficient evidence to establish a causal relationship between human exposure to the substance and subsequent development toxic effects in the progeny.*

Category 2:

- (a) *Substances which should be regarded as if they impair fertility in humans. There is sufficient evidence to provide a strong presumption that human exposure to the substance may result in impaired fertility on the basis of:*
 - (i) *clear evidence in animal studies of impaired fertility in the absence of toxic effects, or evidence of impaired fertility occurring at around the same dose levels as other toxic effects but which is not a secondary non-specific consequence of the other toxic effects;*
 - (ii) *other relevant information.*

(b) *Substances which should be regarded as if they cause developmental toxicity to humans. There is sufficient evidence to provide a strong presumption that human exposure to the substance may result in developmental toxicity, generally on the basis of:*

- (i) *clear results in appropriate animal studies where effects have been observed in the absence of signs of marked material toxicity, or at around the same dose levels as other toxic effects but which are not a secondary non-specific consequence of the other toxic effects;*
- (ii) *other relevant information.*

Category 3:

(a) *Substances which cause concern for human fertility, generally on the basis of:*

- (i) *results in appropriate animal studies which provide sufficient evidence to cause a strong suspicion of impaired fertility in the absence of toxic effects, or evidence of impaired fertility occurring at around the same dose levels as other toxic effects, but which is not a secondary non-specific consequence of the other toxic effects, but where the evidence is insufficient to place the substance in Category 2;*
- (ii) *other relevant information.*

(b) *Substances which cause concern for humans owing to possible developmental toxic effects, generally on the basis of:*

- (i) *results in appropriate animal studies which provide sufficient evidence to cause a strong suspicion of developmental toxicity in the absence of signs of marked maternal toxicity, or at around the same dose levels as other toxic effects but which are not a secondary non-specific consequence of the other toxic effects, but where the evidence is insufficient to place the substance in Category 2;*
- (ii) *other relevant information.*

The risk phrases applicable to substances toxic for reproduction Category 1 and 2 are:

R60 *May impair fertility*

R61 *May cause harm to the unborn child*

Those which apply to substances toxic for reproduction Category 3 are:

R62 *Possible risk of impaired fertility*

R63 *Possible risk of harm to the unborn child*

C10.3 Limiting Concentrations

"Toxic for reproduction" has specified concentration limits, set out in Article 2 of EWC 2002, above which a waste would be hazardous:

- one substance toxic for reproduction of category 1 or 2 classified as R60, R61 at a concentration $\geq 0.5\%$; and
- one substance toxic for reproduction of category 3 classified as R62, R63 at a concentration $\geq 5\%$.

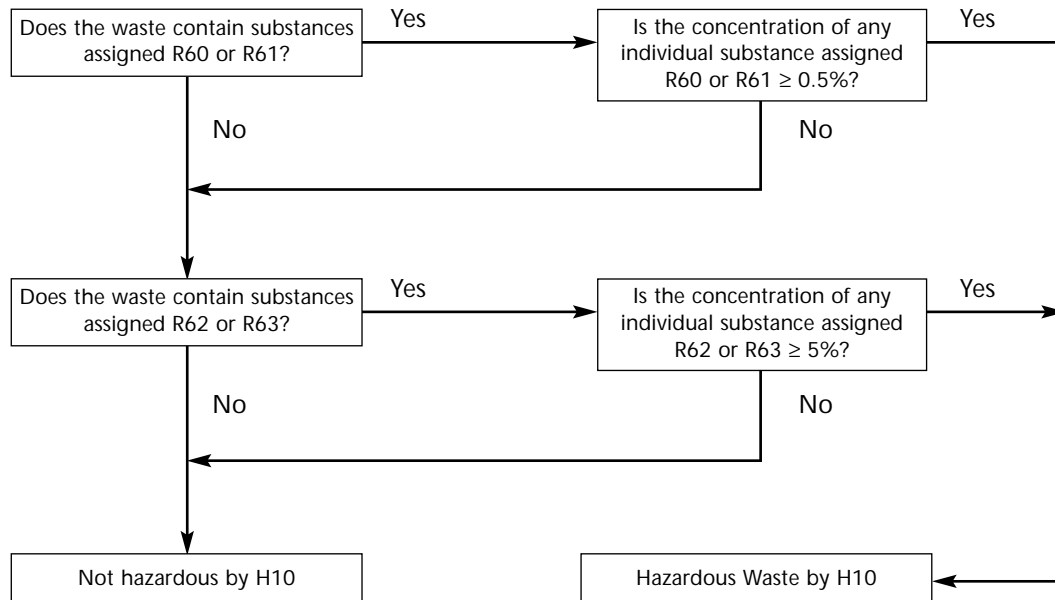
Wastes containing substances classified as toxic for reproduction Category 1 or 2 (i.e. substances with risk phrases R60 or R61) will be hazardous if the concentration of any one of those substances is $\geq 0.5\%$ w/w in the waste. It should be noted that this is a change from the classification under the Special Waste Regulations 1996, under which only substances assigned R61 were classified as special waste because effects on fertility were not considered.

Wastes containing substances classified as toxic for reproduction Category 3 (i.e. substances with risk phrases R62 or R63) will be hazardous if the concentration of any one of those substances is $\geq 5\%$ w/w in the waste. It should be noted that this is a change from the classification under the Special Waste Regulations 1996, under which only substances assigned R63 were classified as special waste because effects on fertility were not considered.

C10.4 Decision Tree

Figure C10.1 sets out the assessment process for the Hazard H10.

Figure C10.1: Decision Tree for the Assessment of Hazard H10



C10.5 Test Methods

None of the EC Annex V test methods corresponds to the definition of "toxic for reproduction".

Some of the alternative tests, such as the Hydra assay and the X-gal assay, have performed well in predicting *in vivo* teratogenic effects. The Hydra assay and X-gal assay tests are summarised below.

C10.5.1 The Hydra Assay

The Hydra assay is a rapid early screening tool for the investigation of the teratogenic potential of compounds and mixtures. The steps for the regeneration of *Hydra attenuata* cell aggregates are performed in three phases with three artificial hydra embryos or three adult hydra placed in each test vessel.

In phase I, the toxicity of the waste is determined by exposing adult hydra to a range of concentrations (log intervals, maximum concentrations 5 mg/ml) and observing at 4, 20, 28, 44, 68, and 92 hours post exposure. Toxicity is assessed by microscopic examination with reference to a standard scoring system. The toxic endpoint is considered to be the "tulip" stage for adults and disintegration for artificial hydra embryos. A concentration resulting in an early toxic endpoint is selected for further study.

In phase II, the minimum effective concentrations in both adult hydra (MECA) and developing embryos (MECD) are determined using a restricted concentration range, based around the concentration obtained from phase I.

The phase II results are subsequently confirmed in phase III by incubating the adult hydra and embryos at the appropriate MEC and two higher or lower concentrations. In phase III the concentrations should be tested in triplicate.

The data are presented in tabular form, and the stage of each hydra/embryo is reported at every observation for each treatment group. The MECs are expressed as an A/D ratio (MEC adult/MEC developing embryo), and a positive result is indicated if this is shown to be significantly less than one on any of the phase III test concentrations. Results obtained using this *in vitro* test have shown good correlations with known teratogens tested *in vivo*.

C10.5.2 The X-Gal Assay

An alternative test uses *Drosophila melanogaster* embryonic cells. The embryonic cells exposed to teratogens dramatically increase their levels of low-molecular weight heat shock proteins (hsp). The test is known as an X-gal assay and has been adapted to be used as teratogen screen for environmental pollutants. Details of the procedure are available in Bournais-Viardibasis *et al* (1983)¹³.

¹³ Bournais-Viardibasis, N., Teplitz, R.R., Chenoff, G.P. and Seecof, R.L. 1983. Detection of teratogens in the *Drosophila* *in vitro* test: Assay of 100 chemicals. *Teratology* 28:109-122.

Appendix C:

C11 Assessment of Hazard H11: Mutagenic

C11.1 Definition

Annex III of the HWD defines H11 "Mutagenic" as:

"substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce hereditary genetic defects or increase their incidence".

C11.2 Risk Phrases

For the purposes of classification and labelling, mutagens are divided into three categories:

Category 1

Substances known to be mutagenic to man. There is sufficient evidence to establish a causal association between human exposure to a substance and heritable genetic damage.

Category 2

Substances which should be regarded as if they are mutagenic to man. There is sufficient evidence to provide a strong presumption that human exposure to the substance may result in the development of heritable genetic damage, generally on the basis of:

- (a) appropriate animal studies,*
- (b) other relevant information.*

Category 3

Substances which cause concern for man owing to possible mutagenic effects. There is evidence from appropriate mutagenicity studies, but this is insufficient to place the substance in Category 2.

The risk phrase applicable to category 1 and 2 mutagenic substances is:

R46 *May cause heritable genetic damage*

The risk phrase applicable to category 3 mutagenic substances¹⁴ is:

R68 *Possible risk of irreversible effects*

C11.3 Limiting Concentrations

"Mutagenic" has specified concentration limits set out in Article 2 of EWC 2002, above which a waste would be hazardous:

- one mutagenic substance of category 1 or 2 classified as R46 at a concentration $\geq 0.1\%$; and
- one mutagenic substance of category 3 classified as R68¹⁵ at a concentration $\geq 1\%$.

¹⁴ R40 for Category 3 mutagens was replaced by R68 by Commission Directive 2001/60/EC.

¹⁵ Article 2 of EWC 2002 specifies the threshold for Category 3 mutagens by referring to substances classified as R40. However, R40 for Category 3 mutagens was replaced by R68 by Commission Directive 2001/60/EC.

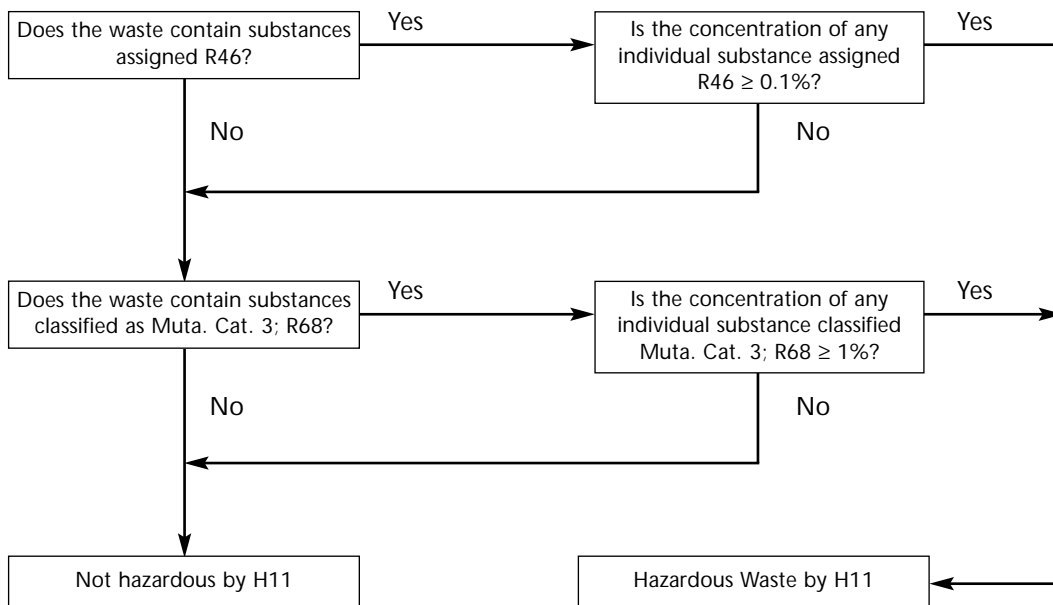
Wastes containing category 1 or 2 mutagens, that is substances with risk phrase R46, will be hazardous if the concentration of any of those mutagens is $\geq 0.1\%$.

Wastes containing category 3 mutagens, that is substances with risk phrases R68, will be hazardous if the concentration of any of those mutagens is $\geq 1\%$. It should be noted that R68 can also be assigned to substance classified as Harmful (H5).

C11.4 Decision Tree

Figure 11.1 sets out the assessment process for the Hazard H11.

Figure C11.1: Decision Tree for the Assessment of Hazard H11



C11.5 Test Methods

The test methods published by the EC that correspond best to the definition of the mutagenic are set out in Table C11.1.

Table C11.1: Test methods for hazard H11

| Test Method | Source | Acceptability |
|--|-------------------------|---------------|
| B10: <i>In vitro</i> mammalian chromosome aberration test | EC Directive 2000/32/EC | ✓ |
| B11: <i>In vivo</i> mammalian bone marrow chromosome aberration test | EC Directive 2000/32/EC | 1 |
| B12: <i>In vivo</i> mammalian erythrocyte micronucleus test | EC Directive 2000/32/EC | 1 |
| B13/14: Reverse mutation test using bacteria | EC Directive 2000/32/EC | ✓ |
| B17: <i>In vitro</i> mammalian cell gene mutation test | EC Directive 92/69/EEC | ✓ |
| Ames Assay | see below | ✓ |
| Mutant <i>Vibrio fischeri</i> Test | see below | ✓ |

Notes:

The Agencies do not endorse destructive animal testing. Wherever there is any doubt about the mutagenic nature of a waste, the precautionary principle should apply.

Tests B10, B13/14 and B17 are *in vitro* tests and are therefore acceptable to the Agencies as non-mammalian test methods to determine hazard H11. Tests B11 and B12 are not considered appropriate because of their reliance on animal testing.

The Ames Assay and the Mutant *Vibrio fischeri* Test are two alternative tests for the hazard H11 providing only a broad classification of potential mutagenic effects. The Ames plate tests use two different strains with and without metabolic activation to detect point mutations in genetically engineered strains of *Salmonella typhimurium*. A clear positive result will give a positive classification. The Ames plate test does not identify the mutagenic potential of metals. A new test has been developed using a dark mutant of *Vibrio fischeri* that exhibits light production when grown in the presence of sublethal concentrations of genotoxic agents. These tests are summarised at the end of this chapter.

C11.5.1 EC Test Method B10 (*In vitro* mammalian chromosome aberration test)

Introduction

Tests on the production of chromosomal aberrations in mammalian cells can provide a preliminary assessment of the mutagenic potential of a substance.

Principle of the test method

The *in vitro* cytogenetic test is a short-term mutagenicity test for the detection of structural chromosomal aberrations in cultured mammalian cells. Cultures of established cell lines as well as primary cell cultures may be used. After exposure to test chemicals with and without an appropriate metabolic activation system, cell cultures are treated with spindle inhibitors such as colchicine to accumulate cells in a metaphase-like stage of mitosis (c-metaphase). Cells are harvested at appropriate times and chromosome preparations are made. Preparations are stained and metaphase cells are analysed for chromosomal abnormalities.

Established cell lines or cultures of primary cells are used, e.g. Chinese hamster cells and human lymphocytes. Test chemicals are prepared in culture medium or dissolved in appropriate vehicles prior to treatment of the cells.

The full test method identifies experimental procedure including details on experimental conditions and controls, culture preparation and conditions, metabolic activation systems, and data evaluation and reporting.

C11.5.2 EC Test Methods B13/14 (Reverse mutation test using bacteria)

Introduction

For the preliminary assessment of mutagenic potential of a substance this method tests the production of gene (point) mutations in microbe cells.

Principles of the test method

The reverse mutation microbial assay measures the base changes in the genome of the organisms by the chemicals it is exposed to. The base change measured for *Escherichia coli* is the tryptophan (trp^- - trp^+) reversion and for *Salmonella typhimurium* the histidine base (his^- - his^+).

Bacteria are exposed to test chemicals with and without metabolic activation. After a suitable period of incubation on minimal medium, revertant colonies are counted and compared to the number of spontaneous revertants in an untreated and/or solvent control culture.

The full test method identifies the preferred bacterial strains for the two species and requires recognised methods of stock culture preparation and storage to be used. In addition the full experimental procedure includes details on bacterial preparation, metabolic activation systems, experimental conditions and controls, and data evaluation and reporting.

C11.5.3 EC Test Methods B17 (*In vitro* mammalian cell gene mutation test)

Introduction

This test can be used to detect gene mutations induced by chemical substances.

Principles of the test method

Mutant frequency is determined by seeding known numbers of cells in medium containing the selective agent to detect mutant cells and in medium without selective agent to determine the cloning efficiency (viability). After a suitable incubation time, colonies are counted. The mutant frequency is derived from the number of mutant colonies in selective medium and the number of colonies in non-selective medium.

The full test method identifies the preferred bacterial strains for the two species and requires recognised methods of stock culture preparations and storage to be used. In addition the full experimental procedure includes details on bacterial preparation, metabolic activation systems, experimental conditions and controls, and data evaluation and reporting.

C11.5.4 The Ames Plate test

The Ames reverse mutation assay has an extensive database, and is a standard test system for mutagenicity. OECD test guidelines are available¹⁶, and the test is included in the Classification, Packaging and Labelling Regulations¹⁷.

This test can be carried out on agar plates or in a liquid medium, which also incorporates a step to simulate the effects of liver enzymes, which may activate some compounds or deactivate others. Waste samples or their extracts should be tested to the limit of toxicity up to a maximum of 5 mg/ml overlay agar. Toxicity is indicated by a clearing of the background lawn, a reduction in the number of spontaneous revertants, or by degree of survival of treated cultures. At least five different amounts of the water sample should be tested, with half-log intervals between plates. The number of revertant colonies per plate is reported for both control and treated series. Individual plate counts, the mean number of revertant colonies per plate and standard deviation should be presented for the tested sample and the controls. The mean data should be summarised graphically.

A positive result in the Ames test does not necessarily demonstrate a hazard, and a negative result on its own does not necessarily give complete confidence that the waste was not mutagenic since it may be important to optimise the test conditions for particular compounds. In general, if at least one of the test series shows a response, leading to at least a doubling of the number of revertants in the control plates, the waste sample or extract may be regarded as mutagenic. Therefore, for the purpose of classification of special waste the test is best used in conjunction with the other screening tests.

The testing of complex mixtures presents a problem: one component may be toxic, but not mutagenic, to the test organisms at such a dose as to prevent the expression of other mutagenic components. Testing of 33 industrial effluents showed that only one sample had sufficient cytotoxic effects to mask mutagenicity. The wide range of effluents tested provides some guidance as to what may be considered to be "high" or "low" Ames responses.

C11.5.5 The Mutant *Vibrio fischeri* Test

This is a test using a dark mutant of *Vibrio fischeri*¹⁸ that produces light when grown in the presence of sublethal concentrations of genotoxic agents.

The mutant bacteria of *Vibrio fischeri* are provided in lyophilised form: they must be rehydrated with double deionised water. Serially diluted samples are then added to each 1 ml of rehydrated bacteria medium for testing. A photometer is used for bioluminescence determination. Prepared samples are measured for light intensity for a continuous 24 hour period at 1 hour intervals. If the luminescence value reached at any time is higher than three times that of a negative control, the test is designated a positive. Duplicate or triplicate samples are run in each test to ensure reliability of results.

The dark mutation bacterium test has some advantages over the Ames test in that it is not affected by the presence of amino acids or other nutrients. Limited validation at this stage suggests that this test should be used in conjunction with the Ames test until further validation has been carried out.

¹⁶ OECD Paris 1984

¹⁷ OJ No. 196 16/8/1967 as amended by Commission Directive 92/69/EEC (OJ No L383 29/12/1992).

¹⁸ Carlsbad, C.A. 1993 Mutatox test data for Prechemicals. Department of Microbics Inc. Wang, W.D., Sun, T.S.C. and Stahr, H.M. 1998 "Continued Elevation and Application of a Bioluminescent Bacterial Genotoxicity Test" in "Advances in Animal Alternatives for Safety and Efficacy Testing" Salem, H. and Katz, S.A. (Eds), Taylor and Francis, USA.

Appendix C:

C12 Assessment of Hazard H12: Produces Toxic Gases in Contact with Water, Air or Acid

C12.1 Definition

Annex III of the HWD defines H12 as:

"Substances and preparations which release toxic or very toxic gases in contact with water, air or an acid".

C12.2 Risk Phrases

One of these risk phrases has to be identified for a substance or preparation in the waste if the waste is to have the potential to exhibit Hazard H12:

R29 *Contact with water liberates toxic gas*

Substances and preparations which in contact with water or damp air evolve very toxic/toxic gases in potentially dangerous amounts. Examples of such substances includes aluminium phosphide and phosphorous pentasulphide.

R31 *Contact with acids liberates toxic gas*

Substances or preparations which react with acid to evolve toxic gases in dangerous amounts. Examples of such substances includes sodium hypochlorite and barium polysulphide.

R32 *Contact with acids liberates very toxic gas*

Substances or preparations which react with acid to evolve very toxic gases in dangerous amounts. Examples of such substances includes salts of hydrogen cyanide, sodium azide.

Any combined risk phrase including R29, R31 or R32 with other risk phrases indicates the potential to exhibit Hazard H12. A special case is the combined risk phrase:

R15/29 *Contact with water liberates toxic, extremely flammable gas*

This risk phrase indicates that Hazard H3A (fifth indent) also applies. The assessment methodology is similar, and the threshold for H3A(v) will be the same as that for H12.

C12.3 Limiting Concentrations

To show Hazard H12, a waste should be capable of releasing a toxic gas at a rate in excess of 1 litre/kg substance/hour. This equates to 1 m³ gas per tonne waste in one hour. It should be assumed that if a substance on the ASL is classified by any of the risk phrases R29, R31 or R32, or could be classified by any of these risk phrases, this criterion will have been met. However, as there are no thresholds for concentrations of R29, R31 or R32 in a waste to make that waste hazardous by H12, it is the waste itself which requires testing, although presence of such substances would indicate the likelihood of the waste possessing H12.

From the listing of substances on the ASL which exhibit this hazard property, the toxic or very toxic gases which could be released by chemical reaction with water, air or an acid appear to be limited at present to those set out in Table C12.1.

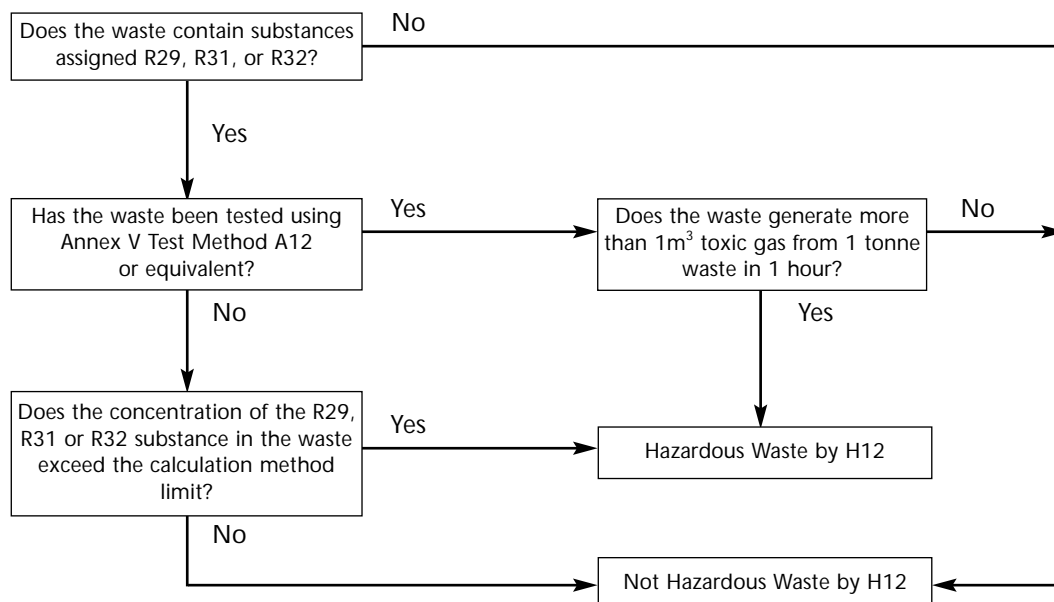
Table C12.1: Some toxic gaseous substances released by H12 waste

| Substance | Chemical Formula | By Risk Phrase(s) | | |
|---------------------------------------|------------------|-------------------|-----|-----|
| | | R29 | R31 | R32 |
| Hydrogen sulphide | H ₂ S | ✓ | ✓ | ✓ |
| Hydrofluoric acid / hydrogen fluoride | HF | ✓ | | ✓ |
| Carbon disulphide | CS ₂ | | ✓ | |
| Sulphur dioxide | SO ₂ | | ✓ | |
| Chlorine | Cl ₂ | | ✓ | |
| Nitrogen dioxide | NO ₂ | | | ✓ |
| Ammonia | NH ₃ | | ✓ | |
| Hydrogen cyanide | HCN | | | ✓ |

C12.4 Decision Tree

Figure C12.1 sets out the assessment process for the Hazard H12.

Figure C12.1: Decision Tree for the Assessment of Hazard H12



C12.4.1 Calculation Method for Hazard H12

This hazard can be determined by calculation or by testing. If information on the composition of the waste is available the calculation method should be used, otherwise EC standard test method A12 or equivalent should be used (see Section C3.6). The threshold concentration is not fixed, but is calculated on the basis of the reaction observed.

The first step in the calculation method is to determine whether the waste contains any of the substances which are classified by the following risk (or combined risk i.e. R15/29) phrases:

R29 *Contact with water liberates toxic gas*

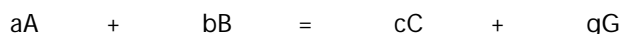
R31 *Contact with acids liberates toxic gas*

R32 *Contact with acids liberates very toxic gas*

The waste producer should also consider what other solid substances in his waste could break down to give off a toxic gas, and carry out the assessment set out in Box H12.1.

Box H12.1: Calculation Method for Hazard H12

1. Write a balanced equation for the reaction that produces the gas. The general form of this equation should be as follows:



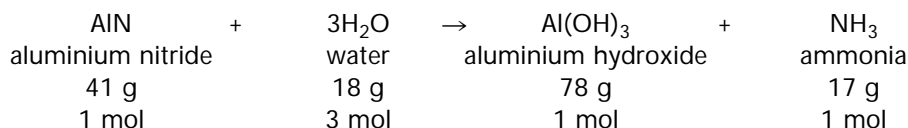
where: A, B, and C are the products and reactants with G being a toxic gas; and

a, b, c and g are the stoichiometric ratios between the products and reactants.

2. Attribute molecular weights and stoichiometric ratios to the substances in the equation.
3. Divide (a x molar weight of A) by (g x 22.4 (the volume of 1 mol of gas at standard temperature and pressure (STP 25°C and 1 atmosphere pressure)). This gives the mass of reactant A that will evolve 1 litre of gas G.
4. The limiting concentration for the substance in the waste with the potential to show hazard H12 is this amount (in grams) divided by 1,000 (to convert to kg) and multiplied by 100 (to give % by weight).

Example Calculation – The main constituents which may make aluminium drosses and slags hazardous are aluminium, aluminium nitride, aluminium carbide. Aluminium nitride is an R29 substance which may make the waste hazardous by H12. The aluminium nitride content may be 0-1% (slag) or 0-10% (dross). Applying this calculation method to the aluminium drosses and slags gives the following threshold limit for H12 (Note: other constituents may make the aluminium drosses and slags hazardous by H3A(v), See Appendix C3).

Aluminium nitride (R29) giving rise to hazard H12



Limiting concentration of aluminium nitride in waste

$$= [(1 \times 41) / (1 \times 22.4) / 1,000] \times 100 = 0.18\% \approx 0.2\%$$

Listed reactions, where known, and threshold concentrations for certain ASL listed substances, with the potential to exhibit for Hazard H12, have been derived using the assessment methodology and are set out in Table C12.2. A substance exhibiting R15/29 also has the potential to exhibit hazard H3A(v), and the threshold limit for that hazard will be the same as that established for H12.

Table C12.2: Examples of substances which may cause a waste to exhibit hazard H12 (Classification by risk phrases R29, R31, R32 and R15/29)

| Substance name | Risk phrases | Equation | Threshold Conc. % ¹ |
|---|--------------|---|--------------------------------|
| Phosphorus pentasulphide | R29 | $P_2S_5 + 8H_2O \rightarrow 5H_2S + 2H_3PO_4$ | 0.1 |
| 3,5-dichloro-2,4-difluorobenzoyl fluoride (DCDFBF) | R29 | $DCDFBF + H_2O \rightarrow HF + \text{Prod.}$ | 1.0 |
| Metam-sodium | R31 | $CH_3NHCSSNa + H^+ \rightarrow CH_3NH_2 + CS_2 + Na^+$ | 0.5 |
| Barium sulphide | R31 | $BaS + 2H^+ \rightarrow H_2S + Ba^{2+}$ | 0.8 |
| Barium polysulphides | R31 | $BaS_n + 2H^+ \rightarrow H_2S + Ba^{2+} + S_{n-1}$ | 0.8 |
| Calcium sulphide | R31 | $CaS + 2H^+ \rightarrow H_2S + Ca^{2+}$ | 0.3 |
| Calcium polysulphides | R31 | $CaS_n + 2H^+ \rightarrow H_2S + Ca^{2+} + S_{n-1}$ | 0.3 |
| Potassium sulphide | R31 | $K_2S + 2H^+ \rightarrow H_2S + 2K^+$ | 0.5 |
| Ammonium polysulphides | R31 | $(NH_4)_2S_n + 2H^+ \rightarrow H_2S + 2NH_4^+ + S_{n-1}$ | 0.3 |
| Sodium sulphide | R31 | $Na_2S + 2H^+ \rightarrow H_2S + 2Na^+$ | 0.4 |
| Sodium polysulphides | R31 | $Na_2S_n + 2H^+ \rightarrow H_2S + 2Na^+ + S_{n-1}$ | 0.4 |
| Sodium dithionite | R31 | $Na_2O_6S_2 + 2H^+ \rightarrow 2Na^+ + SO_2 + H_2SO_4$ | 0.9 |
| Sodium hypochlorite, solution % Cl active ² | R31 | $2NaOCl + 2H^+ \rightarrow Cl_2 + 2Na^+ + H_2O$ | 2.9 |
| Calcium hypochlorite % Cl active ² | R31 | $Ca(OCl)_2 + 2H^+ \rightarrow Cl_2 + Ca^{2+} + H_2O$ | 0.6 |
| Dichloroisocyanuric acid | R31 | $C_3HCl_2N_3O_3 + 2H^+ \rightarrow C_3H_3N_3O_3 + Cl_2$ | 0.9 |
| Dichloroisocyanuric acid, sodium salt of | R31 | $C_3Cl_2N_3O_3Na + 3H^+ \rightarrow C_3H_3N_3O_3 + Cl_2 + Na^+$ | 1.0 |
| Sodium dichloroisocyanurate, dihydrate | R31 | $C_3Cl_2N_3O_3Na + 3H^+ + 2H_2O \rightarrow C_3H_3N_3O_3 + Cl_2 + Na^+ + 2H_2O$ | 1.1 |
| Trichloroisocyanuric acid | R31 | $2C_3Cl_3N_3O_3 + 6H^+ \rightarrow 2C_3H_3N_3O_3 + 3Cl_2$ | 0.7 |
| Hydrogen cyanide, salts of (with the exception of complex cyanides such as ferrocyanides, ferricyanides and mercuric oxycyanide) | R32 | $NaCN + H^+ \rightarrow HCN + Na^+$ | 0.2 |

| Substance name | Risk phrases | Equation | Threshold Conc. % ¹ |
|---------------------|---------------------|--|--------------------------------|
| Sodium fluoride | R32 | $\text{NaF} + \text{H}^+ \rightarrow \text{HF} + \text{Na}^+$ | 0.2 |
| Sodium azide | R32 | $\text{NaN}_3 + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{NO}_2 + \text{NH}_3 + \text{Na}^+$ | 0.3 |
| Aluminium phosphide | R32 | $\text{AlP} + 3\text{H}^+ \rightarrow \text{PH}_3 + \text{Al}^{3+}$ | 0.3 |
| Trizinc diphosphide | R32 | $\text{Zn}_3\text{P}_2 + 6\text{H}^+ \rightarrow 2\text{PH}_3 + 3\text{Zn}^{2+}$ | 0.6 |
| Calcium cyanide | R32 | $\text{Ca}(\text{CN})_2 + 2\text{H}^+ \rightarrow 2\text{HCN} + \text{Ca}^{2+}$ | 0.2 |
| Cadmium cyanide | R32 | $\text{Cd}(\text{CN})_2 + 2\text{H}^+ \rightarrow 2\text{HCN} + \text{Cd}^{2+}$ | 0.4 |
| Calcium phosphide | R15/29 ³ | $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{PH}_3 + 3\text{Ca}(\text{OH})_2$ | 0.4 |
| Aluminium phosphide | R15/29 ³ | $\text{AlP} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + \text{Al}(\text{OH})_3$ | 0.3 |
| Magnesium phosphide | R15/29 ³ | $\text{Mg}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{PH}_3 + 3\text{Mg}(\text{OH})_2$ | 0.3 |
| Trizinc diphosphide | R15/29 ³ | $\text{Zn}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{PH}_3 + 3\text{Zn}(\text{OH})_2$ | 0.6 |

Notes:

¹ Rounded to one decimal place

² Based on 29.3 g (NaOCl)/100ml (max solubility)

³ Contact with water liberates toxic, extremely flammable gas (also exhibit hazards H3A(v))

The hazard is not limited to substances listed on the ASL. These and other gases could also be produced from non-listed substances. The waste producer should consider what substances in the waste could react with water, air or an acid to give off toxic gases, and carry out the assessment.

If there is any doubt as to the potential of a waste to liberate a toxic or very toxic gas, a test can be performed as described in Section C12.5.

C12.5 Test Methods

The approved methods for determining Hazard H12 properties are set out in Table C12.3 with details of the test methods provided in Section C3.6.

Table C12.3: Hazard H12 with associated risk phrases and summary of relevant test methods

| Phase | Risk phrase | Test |
|-------------------------|-------------|---|
| Liquid/solid can | R29 | 1. Directive 92/62/EEC, Test Method A12 (A similar test is used for classification under the Transport of Dangerous Goods Regulations; details and guidance on the tests be obtained from the Health and Safety Executive.) |
| | R31 | 1. Modification of Directive 92/62/EEC Test Method A12. Replace water with an acid which will not cause a displacement reaction to occur. 2. Method for measuring SO ₂ evolved when a waste is in contact with an acid, Environment Agency SWEN 068 |
| | R32 | Modification of Directive 92/62/EEC Test Method A12. Replace water with an acid which will not cause a displacement reaction to occur. |

Appendix C:

C13 Assessment of Hazard H13: Can the Substance Produce Another Hazardous Substance after Disposal?

C13.1 Definition

Annex III of the HWD defines H13 as:

"substances and preparations capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above"

i.e. that could produce another substance which would exhibit one or more of the hazards H1 to H12.

C13.2 Risk Phrases

The hazard applies if the waste contains substances that degrade to form; (or react with) other wastes or substances to produce; (or produce on combustion) other substances with any of the properties H1 to H12, at or above the appropriate threshold concentrations. H13 does not cover reactions which yield materials which are ecotoxic (hazard H14).

H13 may arise from reaction with a substance which is already allocated a risk phrase, or a substance may be produced which may be allocated a risk phrase. Most risk phrases are assigned to hazards already, so the likelihood of a hazard H13 arising by this route is small. However, there are a number of unassigned or associated risk phrases which may cause hazard H13 to arise.

The most likely are:

- R1 *Explosive when dry*
- R4 *Forms very sensitive explosive metal compounds*
- R5 *Heating may cause explosion*
- R6 *Explosive with or without contact with air*
- R16 *Explosive when mixed with oxidising material*
- R18 *In use may form flammable/explosive vapour-air mixture*
- R19 *May form explosive peroxides*
- R44 *Risk of explosion if heated under confinement*

C13.3 Typical Substances

Some examples of wastes and treatment routes which could give rise to H13 are:

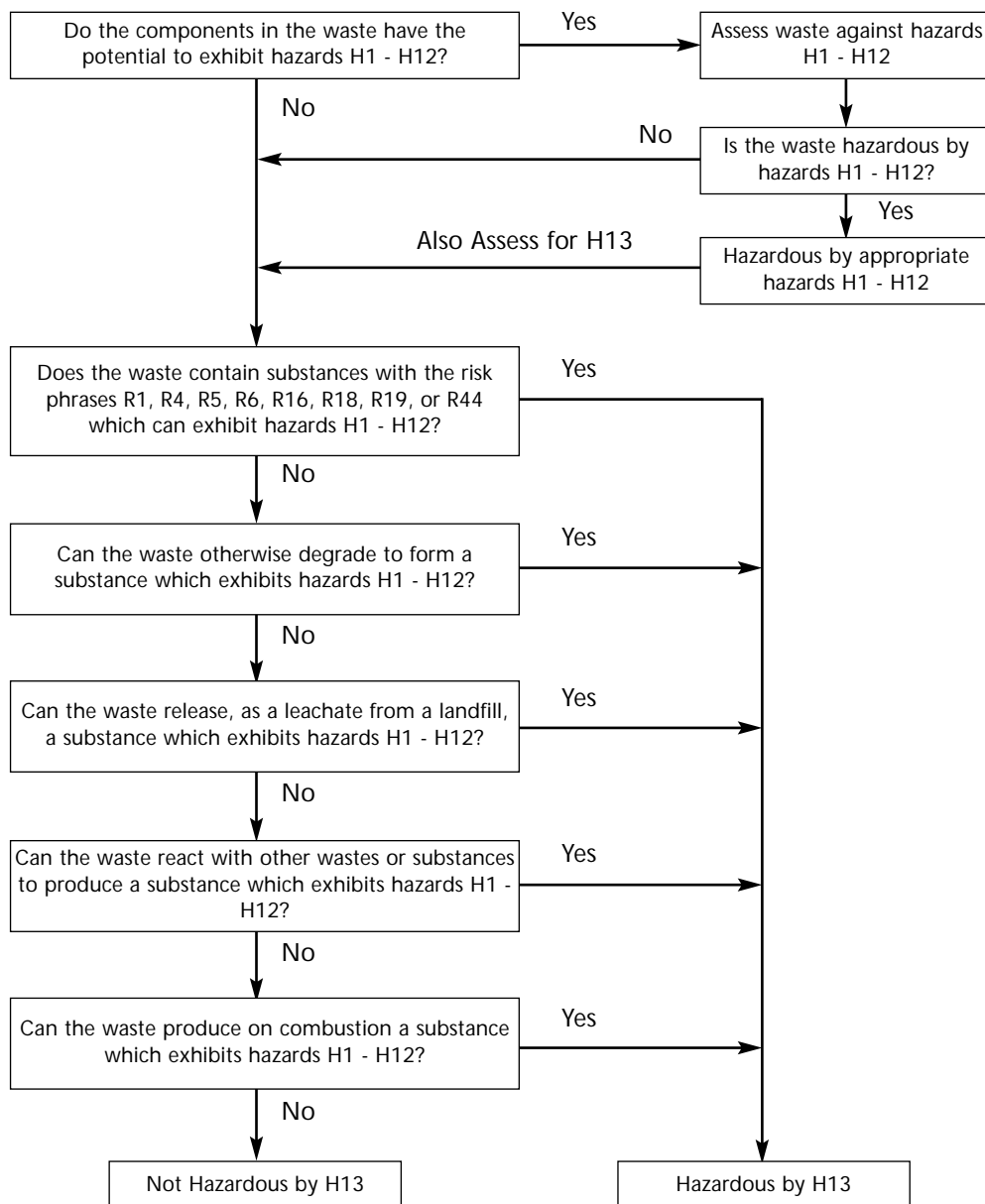
- **Storage.** This may apply to substances with the risk phrases listed above. However, most explosive substances and preparations are not directive or controlled waste, and the assessment process should take into account whether the term "explosive" is used in the strict sense (the definition of the 1875 Act) or more loosely (e.g. R19, where peroxides are oxidising substances and the term explosive relates to the extreme rate of reaction).

- Incineration. This may apply, for example, to organic wastes containing chlorine that in uncontrolled combustion liberate hazardous amounts of dioxins (very toxic, hazard H6) or hydrochloric acid (corrosive, hazard H8).
- Accidental mixing of incompatible materials during chemical treatment. This may apply, for example, to aluminium wastes treated with alkali metal hydroxide solutions, when hydrogen gas is produced (flammable, hazard H3).
- Landfill, anaerobic digestion or composting. The chemical composition of leachates/digestates produced by these disposal routes is normally below threshold levels for other hazards.

C13.4 Decision Tree

Figure C13.1 sets out the assessment process for the Hazard H13.

Figure C13.1: Decision Tree for the Assessment of Hazard H13



C13.5 Test Methods and Limiting Concentrations

The test methods and limiting concentrations for hazards H1–H12 are set out in Appendices C1–C12.

For certain substances and preparations the limiting concentrations for hazard H13, may be calculated from the expected reaction and the likely concentration or production rate of new substance that will be produced. This can then be assessed against the available limits for hazards H1 to H12.

In the case of waste combustion, the likely products may be evaluated and concentrations estimated. The combustion product of the waste can be assessed for hazards H1 to H12.

Appendix C:

C14 Assessment of Hazard H14: Ecotoxicity

C14.1 Definition

Annex III of the HWD defines H14 “Ecotoxic” as:

“substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment”.

The EWC 2002 does not link “Ecotoxic” to any risk phrases or provide specific concentration limits. However, the Dangerous Preparation Directive (DPD) sets out the meaning of “dangerous to the environment”:

“substances and preparations which are dangerous for the environment: substances and preparations which, were they to enter the environment, would or could present an immediate or delayed danger for one or more components of the environment.”

Therefore, as the definitions of substances and preparations which are “dangerous for the environment” from the DPD and “ecotoxic” from the HWD are similar, the classification criterion for ecotoxic has been based on the criterion for “dangerous for the environment” in the DPD. This is consistent with the approach used in the EWC 2002 for the hazardous properties H4 to H8, H10 and H11, where the limiting concentrations for these hazards are based on the concentration limits laid down in the DPD.¹⁹

The DPD specifies concentration limits for ecotoxic substances within preparations; these concentrations are used as the basis of the threshold concentrations for substances within a waste.

C14.2 Risk Phrases

The risk phrases associated with the ecotoxic are broken down into hazards to the aquatic environment and hazards to the non-aquatic environment:

Aquatic Environment

R50 *Very toxic to aquatic organisms*

R51 *Toxic to aquatic organisms*

R52 *Harmful to aquatic organisms*

R53 *May cause long-term effects in the aquatic environment*

Combined or joint risk phrases are common for substances that are dangerous to the aquatic environment; the six possible classification combinations and are set out in Section C14.3 along with the classification criteria.

¹⁹ The footnote to Article 2 of EWC 2002 sets out the basis for the term “classified” and states: “The classification as well as the R numbers refer to Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances (OJ L 196, 16.8.1967, p.1.) and its subsequent amendments. The concentration limits refer to those laid down in Directive 88/379/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations (OJ L 187, 16.7.1988, p.14.) and its subsequent amendments.

Non-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*

Substances which on the basis of the available evidence concerning their properties, persistence, potential to accumulate and predicted or observed environmental fate and behaviour may present a danger, immediate or long-term and/or delayed, to the structure and/or functioning of natural ecosystems other than those covered above.

Detailed criteria still to be determined by the Commission

R59 *Dangerous for the ozone layer*

Substances which on the basis of the available evidence concerning their properties and their predicted or observed environmental fate and behaviour may present a danger to the structure and/or functioning of the stratospheric ozone layer. This includes the substances which are listed in Annex I to Council Regulation (EC) No 2037/2000 on substances that deplete the ozone layer and its subsequent amendments.

C14.3 Classification for the Aquatic Environment

There are six possible classification combinations:

N, R50 *Very toxic to aquatic organisms*

Acute toxicity: 96 hr LC₅₀ (for fish): ≤ 1 mg/l; **or**
48 hr EC₅₀ (for daphnia): ≤ 1 mg/l; **or**
72 hr IC₅₀ (for algae): ≤ 1 mg/l

N, R50-53 *Very toxic to aquatic organisms and may cause long-term effects in the aquatic environment*

Acute toxicity: 96 hr LC₅₀ (for fish): ≤ 1 mg/l; **or**
48 hr EC₅₀ (for daphnia): ≤ 1 mg/l; **or**
72 hr IC₅₀ (for algae): ≤ 1 mg/l

and

the substance is not readily degradable **or**

the log Pow (log octanol/water partition coefficient) ≥ 3.0 (unless the experimentally determined bioconcentration factor (BCF) ≤ 100).

N, R51-53 *Toxic to aquatic organisms and may cause long-term effects in the aquatic environment*

Acute toxicity: 96 hr LC₅₀ (for fish): 1 mg/l < LC₅₀ ≤ 10 mg/l; **or**
48 hr EC₅₀ (for daphnia): 1 mg/l < EC₅₀ ≤ 10 mg/l; **or**
72 hr IC₅₀ (for algae): 1 mg/l < IC₅₀ ≤ 10 mg/l

and

the substance is not readily degradable **or**

the log Pow ≥ 3.0 (unless the experimentally determined BCF ≤ 100).

R52-53 *Harmful to aquatic organisms and may cause long-term effects in the aquatic environment*

Acute toxicity: 96 hr LC₅₀ (for fish): 10 mg/l < LC₅₀ ≤ 100 mg/l; **or**
48 hr EC₅₀ (for daphnia): 10 mg/l < EC₅₀ ≤ 100 mg/l; **or**
72 hr IC₅₀ (for algae): 10 mg/l < IC₅₀ ≤ 100 mg/l

and

the substance is not readily degradable.

R52 *Harmful to aquatic organisms*

Substances **not** falling under the criteria listed above, but which on the basis of the available evidence concerning their toxicity may nevertheless present a danger to the structure and/or functioning of aquatic ecosystems.

R53 *May cause long-term effects in the aquatic environment*

Substances **not** falling under the criteria listed above, but which on the basis of the available evidence concerning their persistence, potential to accumulate, and predicted or observed environmental fate and behaviour may nevertheless present a long-term and/or delayed danger to the structure and/or functioning of aquatic ecosystems.

For example, poorly water soluble substances, i.e. substances with a solubility of less than 1 mg/l, will be covered by these criteria if:

the substance is not readily degradable; **or**

the log Pow ≥ 3.0 (unless the experimentally determined BCF ≤ 100).

C14.3.1 Additive effects for aquatic toxicity

Under the DPD, some of the risk phrases associated with aquatic toxicity are additive i.e. the concentrations of substances with the same and/or different risk phrases need to be added together to determine the correct classification for a preparation and subsequently the threshold concentration for determining whether the waste is hazardous by ecotoxicity. The combinations of additive effects are complex. Table C14.1 summarises the additive effects along with the risk phrases of the resulting preparations. The application of these additive effects to the classification of hazardous wastes is set out in Section C14.4 and Table C14.2.

Table C14.1: Summary of Aquatic Toxicity Additive Effects (for information)

| Preparation Risk Phrase | Criteria for assigning Risk Phrase to a preparation |
|-------------------------|---|
| N: R50–53 | 1. The total concentration of substances classified as N: R50–53 \geq 25% |
| N: R51–53 | 1. The total concentration of substances classified as N: R50–53 \geq 2.5% but < 25%; or 2. The total concentration of substances classified as N: R51–53 \geq 25%; or 3. $[(\text{total conc. N: R50–53}/2.5) + (\text{total conc. N: R51–53}/25)] \geq 1$ |
| R52–53 | 1. The total concentration of substances classified as N: R50–53 \geq 0.25% but < 2.5%; or 2. The total concentration of substances classified as N: R51–53 \geq 2.5% but < 25%; or 3. The total concentration of substances classified as R52–53 \geq 25%; or 4. $[(\text{total conc. N: R50–53}/0.25) + (\text{total conc. N: R51–53}/2.5) + (\text{total conc. R52–53}/25)] \geq 1$ |
| N: R50 | 1. The total concentration of substances classified as N: R50 \geq 25%; or 2. $[(\text{total conc. N: R50–53}/25) + (\text{total conc. N: R50}/25)] \geq 1$ |
| R52 | 1. The total concentration of substances classified as R52 \geq 25%; |
| R53 | 1. The total concentration of substances classified as R53 \geq 25%; or 2. $[(\text{total conc. N: R50–53}/25) + (\text{total conc. N: R51–53}/25) + (\text{total conc. R52–53}/25) + (\text{total conc. R53}/25)] \geq 1$ |

Note:

all concentrations are percentages by weight.

C14.4 Limiting Concentrations

C14.4.1 Criteria for classifying a waste as ecotoxic on the basis of aquatic toxicity

When considering wastes, the purpose is to identify whether that waste is dangerous to the environment or ecotoxic. The combinations of additive effects set out in Table C14.1 can be simplified. The simplified criteria are set out in Table C14.2, which details the threshold levels for classifying a waste as ecotoxic on the basis of aquatic toxicity.

Table C14.2: Criteria for classifying a waste as ecotoxic on the basis of aquatic toxicity

| | | | | | | | |
|--|---|--|-----------|--|----------|--------------------------|-----------|
| 1. For acute aquatic toxicity and long-term adverse effects, a waste will be hazardous if: | | | | | | | |
| $\frac{\sum \text{N: R50-53 Subst.}}{0.25}$ | + | $\frac{\sum \text{N: R51-53 Subst.}}{2.5}$ | + | $\frac{\sum \text{R52-53 Subst.}}{25}$ | ≥ 1 | | |
| 2. For acute aquatic toxicity, a waste will be hazardous if: | | | | | | | |
| $\sum \text{N: R50-53 Subst.}$ | + | $\sum \text{N: R50 Subst.}$ | ≥ 25 | | | | |
| 3. For long-term adverse effects, a waste will be hazardous if: | | | | | | | |
| $\sum \text{N: R50-53 Subst.}$ | + | $\sum \text{N: R51-53 Subst.}$ | + | $\sum \text{R52-53 Subst.}$ | + | $\sum \text{R53 Subst.}$ | ≥ 25 |
| 4. For aquatic toxicity, a waste will be hazardous if: | | | | | | | |
| $\sum \text{R52 Substances} \geq 25$ | | | | | | | |
| Σ = total concentration as w/w per cent | | | | | | | |

C14.4.2 Criteria for classifying a waste as ecotoxic on the basis of terrestrial non-aquatic toxicity

Criteria for preparations containing substances with risk phrases relating to the terrestrial environment, i.e. R54 to R58, are not currently included in the DPD. The classification of preparations using these risk phrases will be included in the DPD when detailed criteria for their use have been developed. Until then, therefore, risk phrases R54 to R58 should not be considered when assessing the ecotoxic hazard of wastes and classifications should be based solely on aquatic toxicity data.²⁰

C14.4.3 Criteria for classifying a waste as ecotoxic on the basis of danger to the ozone layer

Substances that are listed in Annex I to Council Regulation (EC) No 2037/2000²¹ on substances that deplete the ozone layer and its subsequent amendments are classified as R59.

For a waste to be classified as ecotoxic on the basis of containing substances identified as: N; R59 or R59 (Dangerous for the ozone layer):

- the concentration of an individual substance classified as N; R59 or R59 must be $\geq 0.1\%$.

The concentrations of substance classified as N; R59 or R59 are not additive.

C14.4.4 Specific Concentration Limits for Highly Ecotoxic Substances

It is necessary to treat certain substances differently due to their pollution potential and persistence in the environment, e.g. polychlorinated biphenyls (PCBs) and polychlorinated terphenyls (PCTs). Therefore specific concentration limits will be set on highly ecotoxic substances based on international agreement.

²⁰ Research has suggested that in the majority of cases possibly with the exception of some pesticides, an assessment of ecotoxic hazard based solely on aquatic toxicity data would result in the same classification as an assessment that included terrestrial effects (OECD series on testing and assessment No. 33).

²¹ OJ L 244, 29.2000, p. 1.

To maintain a consistency with international and UK legislation and guidance, the Agencies consider that the level of 50 mg/kg should be the defining threshold concentration for wastes containing PCBs and PCTs: at or above this concentration such waste should be considered as hazardous waste.

At present, there are no other internationally agreed limits for any other substance. In the future, specific individual thresholds for other highly polluting substances will be set, based on international agreements, as with PCBs and PCTs. It is proposed that when such limits are set, they will be adopted for the purpose of hazardous classification.

C14.4.5 Metals and Metal Compounds

The characterisation of metals and metal compounds is complex and international consensus on specific criteria is still being developed. However, the DPD does not exclude metals and metal compounds from the evaluation of the environmental hazards of preparations. Therefore until international consensus is achieved and to ensure consistency with the DPD, metals and metal compounds should be included in ecotoxic assessments.

However, the EWC 2002 excludes from the classification process pure metal alloys, that are not contaminated by dangerous substances, (see Paragraph 7 of Annex to EWC 2002).

C14.5 Procedure for Assessment of Hazards H14

First, determine whether the waste contains any substances classified with the risk phrases N: R50, N: R50-53, N: R51-53, R52, R52-53, R53 or R59, using the ASL or other data sources. If it does and the concentrations within the waste equal or exceed the relevant thresholds the waste will be hazardous.

It must be remembered that:

- the concentrations of substances with aquatic toxicity risk phrases may be additive (see Table C14.1);
- the concentrations of substances with aquatic toxicity risk phrases cannot be added to the concentrations of substances classified N; R59 or R59; and
- the concentrations of substance classified as N; R59 or R59 are not additive.

Secondly, determine if the waste contains any highly ecotoxic substances with specific concentration limits. At present this only covers PCBs and PCTs, which have a threshold of 0.005% (50 mg/kg).

Using testing

Testing should be limited to the cases where the hazards cannot be adequately determined from the composition of the waste, i.e.:

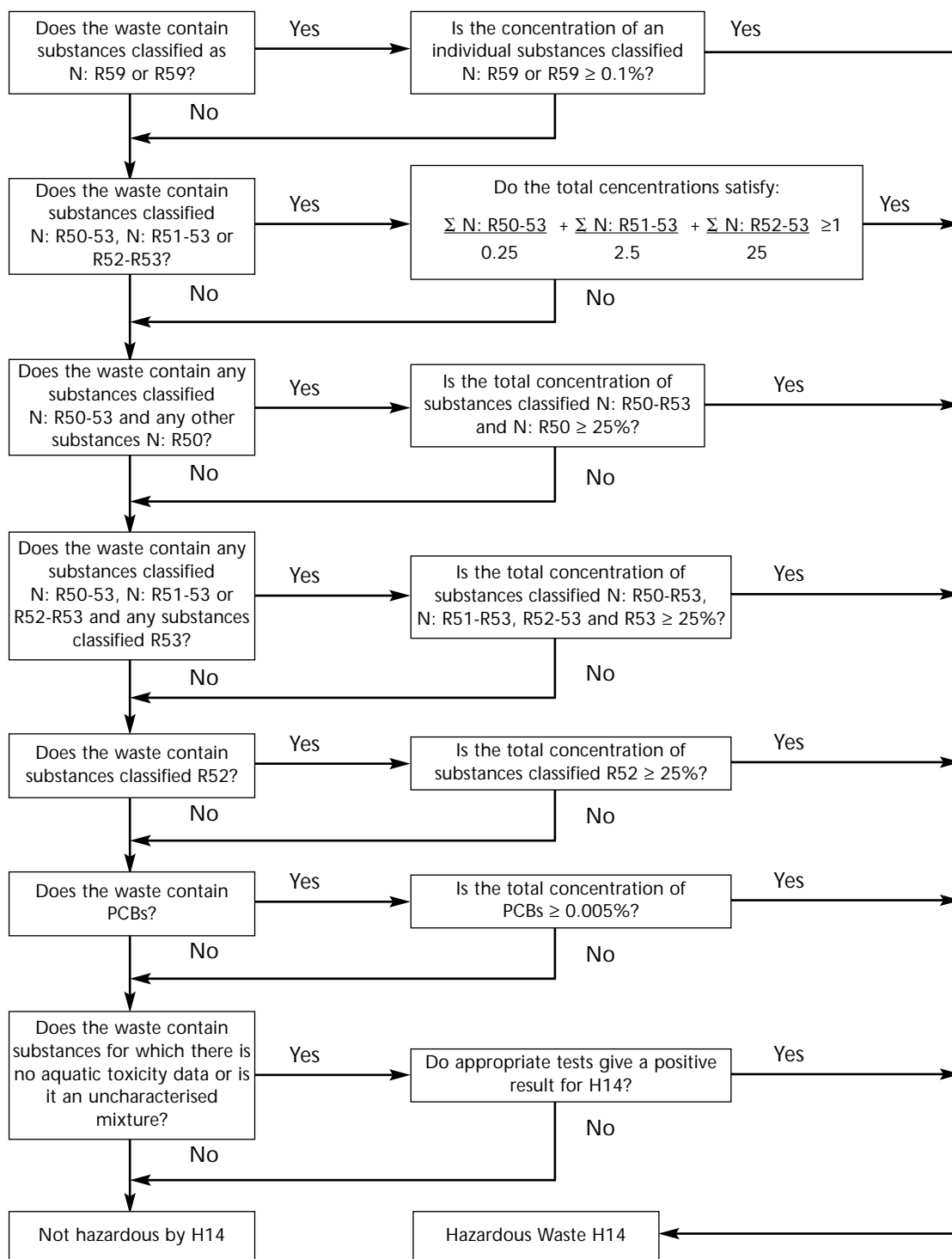
- where the waste contains substances for which there is no aquatic toxicity data; or
- where the waste is an uncharacterised mixture (i.e. where there is no, or incomplete, chemical analysis and/or where there is reason to believe that the waste may contain unknown substances or breakdown products).

Details of the test methods for hazards H14 can be found in Section C14.7.

C14.6 Decision Tree

Figure C14.1 sets out the assessment process for Hazards H14.

Figure C14.1: Decision Tree for the Assessment of Hazard H14



C14.7 Test Methods

Aquatic toxicity testing of wastes presents particular problems and, as a result, there is on-going debate over the most appropriate methods. For the interim the following test regime is proposed for assessing a waste whose classification cannot be determined by calculation, for Hazard H14.

C14.7.1 Aquatic Toxicity Testing Regime

The aim of the test regime is to determine for complex waste, which contains substances for which there is no aquatic toxicity data or where the waste is an uncharacterised mixture, whether the waste should be classified as ecotoxic, while limiting the need for testing higher aquatic species (e.g. fish).

The regime is based on toxicity testing the water-accommodated fraction (WAF) of a waste using aquatic toxicity testing methods. The WAF is an aqueous fraction containing the dissolved and/or suspended and/or emulsified fraction of waste, which is prepared using a standard loading rate and mixing regime. The WAF would then be limit tested at 100% using both:

- *Daphnia magna*, 48-hr, acute lethality test; and
- Algal 72-hr, growth inhibition test.²²

If the observed effect, relative to appropriate controls, during the testing of the 100% WAF is $\geq 50\%$ (i.e. 50% of *Daphnia* are immobilised or there is a 50% reduction in growth or growth rate) the waste would be classified as hazardous by H14 ecotoxic.

Additional testing using fish may be necessary when both algae and daphnia results are close to the threshold. In such cases guidance on the appropriate tests should be obtained from the Agencies.

C14.7.2 Terrestrial Toxicity Testing Regime

Where there is reason to believe that a waste contains substances that only have effects on the terrestrial environment, guidance on the appropriate terrestrial test methods should be obtained from the Agencies.

C14.7.3 Preparation of Water-Accommodated Fraction (WAF)

The WAF should be prepared in accordance with OECD Guidance Document on Aquatic Toxicity Testing of Difficult Substances²³, with the following preparation requirements set out in Table C14.3.

²² Where testing using algae cannot be used (i.e. due to colour/particulate etc interfering with either the growth or measurement of growth) aquatic toxicity testing using Duckweed (*Lemna minor*) may be an appropriate substitute.

²³ OECD Environmental Health and Safety Publications, Series on Testing and Assessment No.23: ENV/JM/MONO(2000)6, June 2000.

Table C14.3: Preparation of Water-Accommodated Fraction requirements

| Parameter | Preparation Requirement |
|------------------|---|
| Loading rate | The ratio of test material to water (in mg/l) used in the preparation of a WAF 100 mg of waste per litre of water |
| Mixing Period | For complex metal wastes 7 days |
| | Other wastes 48 hrs |
| Mixing Procedure | Waste introduced into vortex of dilution medium created by magnetic stirrer in aspirator. Stirring should be sufficiently vigorous to create a vortex |
| Standing Period | 1 hour then draw off WAF from aspirator, with undissolved or undispersed waste removed |

C14.7.4 EC Test Method C2 (Acute toxicity for Daphnia) for Hazard H14

Introduction

The purpose of this test is to determine the median effective concentration of the WAF of a waste for immobilisation (EC₅₀) of Daphnia in fresh water.

Definitions and units

The Directive requirement for the LC₅₀ for Daphnia is considered to be fulfilled by the determination of the EC₅₀ as described in this test method. Acute toxicity is expressed in this test as the median effective concentration (EC₅₀) for immobilisation. This is the concentration, in terms of initial values, which immobilises 50% of the Daphnia in a test batch within a continuous period of exposure, which must be stated.

Principle of the test method

A limit test is performed at 100 % WAF in order to demonstrate that the EC₅₀ is greater than or less than this concentration.

Detailed procedures are given in the full test method which comprehensively covers test performance, apparatus, solutions, reference substances, quality criteria and data evaluation and interpretation.

Test organism

Daphnia magna is the preferred test species although *Daphnia pulex* is also permitted. Requirements for the stock to be used are given in the full method.

C14.7.5 EC Test Method C3 (Algal inhibition test) for Hazard H14

Introduction

The purpose of this test is to determine the effects of the WAF of a waste on the growth of a unicellular green algal species. Relatively brief (72 hours) tests can assess effects over several generations. This method can be adapted for use with several unicellular algal species, in which case a description of the method used must be provided with the test report.

This method is most easily applied to water-soluble substances, that under the conditions of the test, are likely to remain in the water. The method can be used for substances that do not interfere directly with the measurement of algal growth.

Definitions and units

The following definitions and units should be used:

- cell density: the number of cells per millilitre;
- growth: the increase in cell density over the test period;
- growth rate: the increase in cell density per unit time;
- EC₅₀: in this method, that concentration of test substance which results in a 50% reduction in either growth (EbC₅₀) or growth rate (ErC₅₀) relative to the control.

Principle of the test method

A limit test is performed at 100% WAF in order to demonstrate that the EC₅₀ is greater than or less than this concentration.

Exponentially growing cultures of selected green algae are exposed to the 100% over several generations under defined conditions. The test solutions are incubated for a period of 72 hours, during which the cell density in each solution is measured at least every 24 hours. The inhibition of growth in relation to a control culture is determined.

Detailed procedure is given in the full test method which comprehensively covers test performance, apparatus, solutions, reference substances, quality criteria and data evaluation and interpretation.

Test organisms

The most appropriate species of green algae used for the culturing and testing in this method are fast-growing species. Preferred species are *Pseudokirchnerella subcapitata* or *Scenedesmus subspicatus*.