SCHOOL OF CIVIL PROTECTION

MODULE BI-2/B

TECHNOLOGICAL RISKS AND EFFECTS

HANDBOOK

ACCORD RISQUES MAJEURS • MAJOR HAZARDS AGREEMENT
EUR-OPA
Conseil de l'Europe · Council of Europe

IOM - OIM

Authors

Victor POYARKOV

Executive Director, Council's of Europe 'European Centre of Technological Safety (TESEC - Kiev)', Kiev, Ukraine

- 1975 - Ph.D. in Nuclear Physics

Alexander A. GOLUB

Associate Professor, Department of Chemistry, “Taras Shevchenko” National University, Kiev, Ukraine

- 1981 – Ph.D. in Chemistry

Oleg GAYDUK

Deputy Minister of Emergency Management, Government of Ukraine, Ukraine

- 1985 - MSc degree in Chemistry

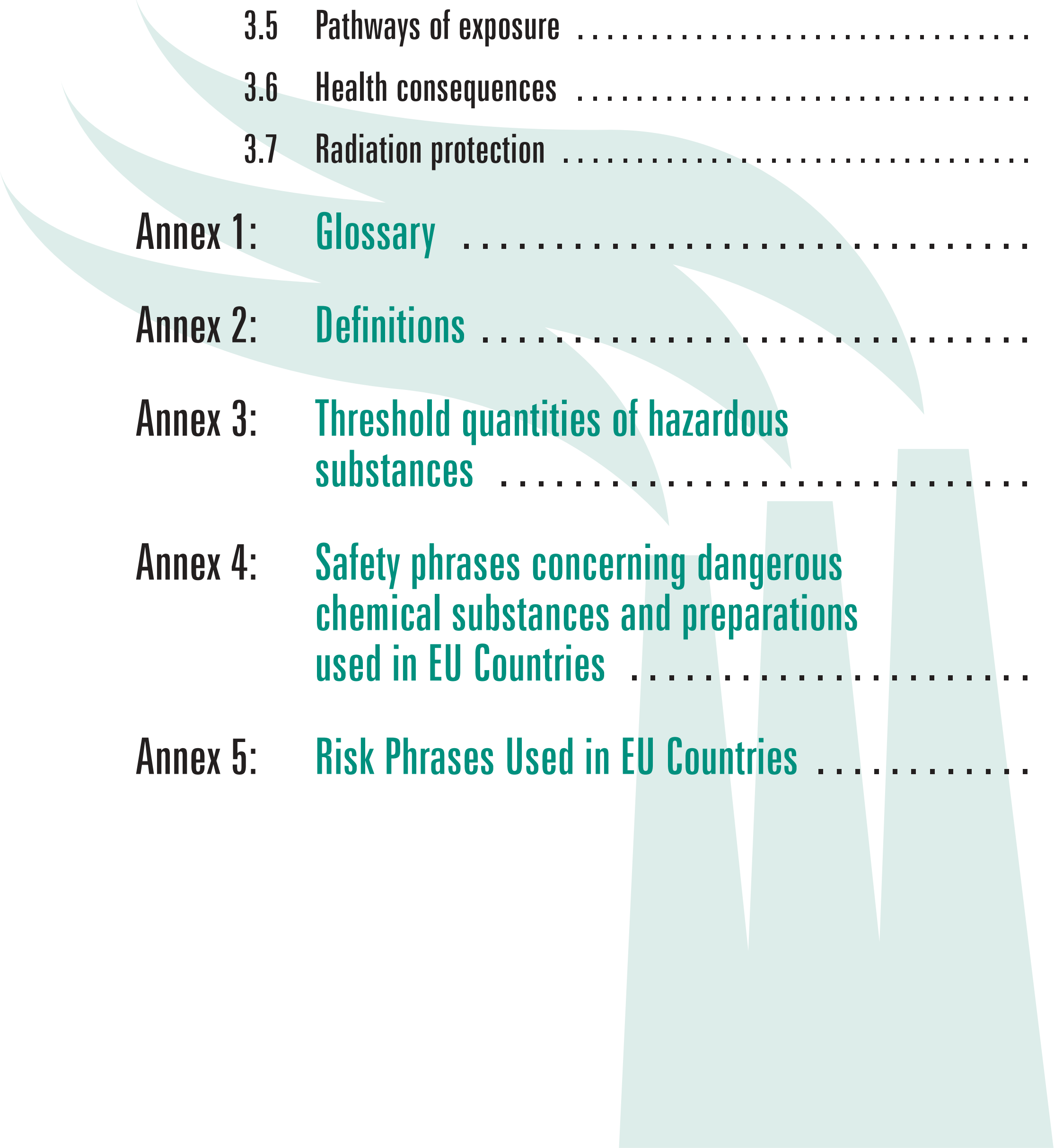
Dmytro HORDYNSKY

Deputy Head, Council’s of Europe *‘European Centre of Technological Safety (TESEC – Kiev)’*, Kiev, Ukraine

- 1995 – MSc degree in Mathematics and Radioecology

TECHNOLOGICAL RISKS AND EFFECTS

Table of contents



1. Introduction

This course has been prepared with the recognition that hazardous substances are present in communities around the world, mainly in industrial facilities and during transport via highways, rail and waterways. Accidents, including fires, explosions and leakages resulting in the release of these substances, can have adverse effects on human health, property and the environment.

Human exposure to hazardous substances can cause injury or even death to a large number of people. Human exposure may occur directly through eye exposure, skin contact, inhalation or ingestion, or as a result of contamination of water or soil, which can affect the food chain.

The population at risk in the event of an accident (or the “potentially affected public”) is, for the most part, either inside or immediately outside an industrial site or near transportation routes, although dispersed populations may be affected through the contamination of water or the food chain. Less frequently, the exposed population may be at some distance from the accident site, possibly in areas across national borders.

For purposes of this course related to technological accident prevention, preparedness and response, the focus is on accidents at fixed installations involving hazardous substances that could affect people, property or the environment, although many provisions also apply to transport accidents. “Fixed installations” are defined broadly as including plants or sites that produce, process, use, handle, store, or dispose of hazardous substances. Thus, fixed installations include facilities of hazardous substances manufacturers, as well as other industrial sites where hazardous substances are used or handled; warehouses containing hazardous substances; disposal facilities; and ports and other designated transport interfaces.

It should be noted that many elements of the community, industry and government are involved in efforts to prevent, prepare for, and respond to chemical or radiological accidents. *The Guiding Principles for Chemical Accident Prevention, Preparedness and Response* prepared by the Organisation for Economic Co-operation and Development (OECD) provide a blueprint for such efforts.

The *Guiding Principles* give an overview of the actions which should be taken by public authorities, industry, labour and other interested parties. To develop the basis for this guidance, the OECD joined with three United Nations bodies which have particular expertise in this subject:

- the International Programme on Chemical Safety (IPCS)
- the United Nations Environment Programme (UNEP)
- the World Health Organisation (WHO)
- the International Labour Office (ILO)

This course is based on three main OECD documents related to chemical accident prevention, preparedness and response:

- *Guiding Principles for Chemical Accident Prevention, Preparedness and Response: Guidance for Public Authorities, Industry, Labour and Others for the Establishment of Programmes and Policies related to Prevention of, Preparedness for, and Response to Accidents Involving Hazardous Substances Areas (1992)*
- *Health Aspects of Chemical Accidents: Guidance on Chemical Accident Awareness, Preparedness and Response for Health Professionals and Emergency of Response Areas (1994)*

- *Guidance concerning Health Aspects of Chemical Accidents. For Use in the Establishment of Programmes and Policies Related to Prevention of, Preparedness for, and Response to Accidents Involving Hazardous Substances (1996)*

Training courses of US Federal Emergency Management Agency are also used.

The aim of this course is to provide guidance to managers and other decision-makers in order to improve prevention of accidents involving hazardous substances which might affect human health and, should an accident occur, to minimize their adverse effects on human health.

1.1 Key Definitions

The terms *“chemical accident”* and *“chemical emergency”* are used to refer to an event or dangerous occurrence resulting in the release of a substance or substances hazardous to human health and/or the environment in the short or the long term. Such events or occurrences include fires, explosions, leakages or releases of toxic substances that can cause illness, injury, disability or death often to a large number of human beings.

While dispersed populations may be affected through contamination of water or the food chain resulting from a chemical , the exposed population is frequently either inside or outside an industrial site. In an urban area, the exposed population may be in the vicinity of a ruptured vehicle that has been transporting hazardous substances. Less frequently, the exposed population is at some distance from the accident site, including possibly areas across national borders. Potentially affected areas in neighbouring countries could include those with limited chemical emergency response plans or capabilities.

This definition needs to be set alongside the concept of a “chemical accident”, in which an exposure arising from releases of a substance or substances may result in illness or the possibility of illness. The number of people affected by a chemical accident may be very few (even just one), and illness, disability or death may occur a considerable time (for example, several years) after the exposure.

In addition to human health effects, chemical accidents may result in extensive or long-term damage to the environment, with considerable human and economic costs.

Key definitions pertinent to this Module are presented in Annexes 1 (glossary) and 2 (definitions).

1.2 Classification of chemical accidents

From the health perspective, there are a number of ways of classifying chemical accidents, none of which is complete or mutually exclusive. For example, classification could be based on:

- the chemical(s) involved, the amount released, their physical form, and where and how the release occurred
- the sources of the release
- the extent of the contaminated area
- the number of people exposed or at risk
- the routes of exposure
- the health or medical consequences of exposure

Chemicals Involved

The chemicals involved in an accident could be grouped according to whether they are:

- dangerous substances (for example, explosives, flammable liquids or solids, oxidizing agents, toxic substances and corrosives)
- additives, contaminants and adulterants (for example, in drinking water, food and beverages, medicines and consumer goods)
- radioactive products

Classification according to the amount of the chemical released should account for its hazardous properties (for example, one kilogram of cyanides is more dangerous than one kilogram of chlorine gas).

Sources of the release

Releases may result from human activity or may be of natural origin.

- *Anthropogenic* sources include manufacture, storage, handling, transport (rail, road, water and pipeline), use and disposal
- Sources of *natural origin* include volcanic and other geological activity, toxins of animal, plant and microbial origin, natural fires and minerals

Extent of the contaminated area

Accidents can be classified according to whether they:

- were contained within an installation and affected no one outside
- affected only the immediate vicinity of an installation
- affected a wide area around an installation
- were highly dispersed, even beyond the country borders

Number of people exposed or at risk

Chemical accidents can be classified by the number of people affected, calculated in terms of deaths, injuries, and/or evacuees. However, the severity of a chemical accident cannot be determined solely on this basis. All the known circumstances and consequences of an accident must be taken into account in assessing its severity.

Pathways of exposure

From the health perspective, routes of exposure can be a means of classifying chemical accidents. There are four main direct routes of exposure:

- inhalation
- eye exposure
- skin contact
- ingestion

None of these routes of exposure is mutually exclusive.

Health or medical consequences

Chemical accidents can also be classified according to the health or medical consequences, or according to the system/organ affected. Examples are accidents giving raise to carcinogenic, dermatological, immunological, hepatic, neurological, pulmonary or teratogenic effects.

1.3 Special features of chemical accidents

In principle, an organisational structure that exists to respond to other types of accidents (for example, natural disasters) can be used in the event of a chemical accident. From the health perspective, however, chemical accidents have several special features. These are outlined below:

- A “pure” chemical exposure (that is human exposure to chemicals without mechanical trauma) can produce a finite number of predictable health effects. Not all victims will have the same collection of effects, which will be dependent on routes of exposure, the duration of exposure and individual susceptibilities.
- There may be a toxic zone that can only be entered by personnel wearing full protective clothing. In principle, ambulance and other medical personnel should never enter such a zone.
- Individuals exposed to chemicals may constitute a risk for rescue personnel, who could become contaminated by the chemicals left on the exposed persons. Therefore, early decontamination should preferably take place before those exposed are given definitive treatment.
- Hospitals (and other treatment facilities) and the roads leading to them may be located in the toxic zone, so that access is blocked and new patients cannot be received for a considerable period of time. Plans should therefore be drawn up for temporary treatment facilities in schools, sports centres, tents, private homes, etc.
- In the case of many chemicals, general knowledge of their properties and effects may not be complete. Effective systems should therefore be identified and established for obtaining essential information on the chemical(s) of concern and providing this information to rescue workers and other persons who need it.
- Inventory activities need to be carried out to identify risks (fixed and mobile), and to identify the resources available for taking care of exposed persons who suffer corrosive and thermal burns and those in need of ventilatory support.
- A number of exposed persons may need to be kept under observation for one or two days even though they do not have symptoms.

Key definitions

Hazardous materials are chemical substances, which, if released or misused, can pose a threat to the environment or health. These chemicals are used in industry, agriculture, medicine, research, and consumer goods. Hazardous materials come in the form of explosives, flammable and combustible substances, poisons and radioactive materials.

Hazardous materials in various forms can cause death, serious injury, long-lasting health effects, and damage to buildings, homes and other property. Many products containing hazardous chemicals are used and stored in homes routinely. These products are also shipped daily on the nation’s highways, railroads, waterways, and pipelines. These substances are most often released as a result of transportation accidents or because of chemical accidents in plants.

2. Chemical and radiological hazards

2.1 Hazardous materials (HM)

The production and use of chemicals are fundamental factors in the economic development of all countries, whether they are industrialised or developing. In one-way or another, chemicals directly or indirectly affect the lives of all humans and are essentials to our feeding (fertilisers, pesticides, food additives, packing), our health (pharmaceuticals, cleaning materials), or our well being (appliances, fuels, etc).

The first and most essential step leading to the safe use of chemicals is to know their identity, their hazards to health and the environment and the means of controlling them. This knowledge should be available with reasonable effort and cost. Furthermore, this inherently complex knowledge must be organised in such a way that essential information on the hazards and corresponding protective measures can be identified and conveyed to the user in a form that is easy to understand.

The hazard classification and labelling process is an essential tool for establishing an effective information transfer so that the degree of the hazard the chemical represents for man and the environment can be recognised, the correct preventive actions be chosen, and safe use established.

International, regional, and national classification and labelling systems are already established and tested in practice.

- *The United Nations Recommendations on the Transport of Dangerous Goods* is widely recognised and used among the UN member states
- An example of a system that has been designed for use in several countries is the classification and labelling system of the European Communities (EC)
- Several functioning national systems, such as those of Canada and the USA, may also be used as models for national systems

This course consists of:

- EC symbols and indications of danger
- EC standard safety phrases (S-phrases, Annex 4)
- EC standard risk phrases (R-phrases, Annex 5)
- UN list of hazard classes for transport of dangerous goods
- UN symbols for transport of dangerous goods
- Other Annexes with useful information

2.2 Important Properties of HM

An understanding of basic chemical and physical properties is important for the HM (HAZMAT) responder. Chemical and physical properties provide the true picture of chemical hazards and may allay much of the hysteria associated with hazardous agents.

2.2.1 States of Matter

Basic chemical properties start with the states of matter. The state that a chemical is in provides some important information about possible tactical objectives that a HAZMAT team may employ to mitigate an accident. Biological agents are typically found in the solid states, but also may be in the liquid state. Chemical and blister agents can be found as solids, liquids, or gases.

Identification of possible agents can be accomplished by the state of matter, as mustard agent is a solid material at 57°F (14°C), and presents little risk in this state of matter. Mustard agent that is above ambient temperature does present a greater risk, predominately through contact.

2.2.2 Concentration

When discussing concentration in chemical and physical property terms, one normally is talking about corrosives. The concentration is the amount of a given substance in another, typically water. As an example, 98 percent sulphuric acid is 98 percent sulphuric acid and 2 percent water, while 20 percent hydrochloric acid has 80 percent water in the mixture.

2.2.3 Melting and freezing point

Melting points and freezing points are interrelated and, in reality, is the same thing. They are not two points. Rather, the temperature is the specific number at which a substance freezes or melts, which we will call the melting-freezing point. In order for a substance to freeze, the temperature must go below the melting-freezing point. In order for the substance to melt, the temperature must go above the melting-freezing point.

Table 1 **Melting and freezing points of some chemicals**

Chemical	Celsius	Fahrenheit
Ethion	-13°	9°
Sulphuric acid	11°	52°
Chlorine	-101°	-150°
Acetone	-95°	-138°
Benzene	6°	42°
Toluene	-96°	-141°

The points at which a material changes from one state of matter to another can be an important tactical consideration. At the melting point, a material goes from the solid state to the liquid state, and at the freezing point, the material goes from the liquid state to the solid state.

For example, you are at a facility that has a leaking valve from a sulphuric acid tank, and the leak is a slow drip from the valve. The cap is unable to stop the flow but it has substantially reduced the amount of product coming from the valve. At the facility they have dry ice, which could be packed around the valve. Given that sulphuric acid freezes at 52°F (11.1°C), packing the valve with dry ice would stop the leak and provide a considerable time cushion to develop a mitigation strategy further, such as locating a vacuum truck to offload the tank.

2.2.4 Boiling point

The boiling point is important because once the product reaches the boiling point, it is moving from the liquid state to the gaseous state. It is defined as the temperature of a liquid at which its vapour pressure is equal to or greater than the atmospheric pressure of the environment. Once a product is in the gaseous state, the ability to cause harm has moved from a predominately contact hazard that is fairly easy to control to an inhalation hazard and the gaseous state, which is difficult to control. Once an agent reaches its boiling point, vapours are being produced and can present a risk to the responder.

2.2.5 Vapour Pressure

It is the ability of the material to produce vapours that can cause humans severe problems. The actual definition is the pressure that is exerted on a container from the vapours coming from the liquid. Chemicals that have high vapour pressures generally are referred to as volatiles. The expression of vapour pressure comes in three forms: pounds per square inch (*psi*), atmospheres (*atm*), and the most commonly used, millimetres of mercury (*mm/Hg*). The average vapour pressures of the atmosphere are presented in Fig. 1.

The use of vapour pressure is fairly common for HAZMAT responders, but it is commonly not understood. If a material has a vapour pressure, it has the ability to cause harm through inhalation and skin contact routes. If the material does not have a vapour pressure or has a low vapour pressure, then the risk to the responder is almost exclusively through actual physical contact If you are trying to mitigate an accident in which a low vapour pressure with a corrosive liquid was released from a drum and is on the ground, then a low level of chemical protective clothing CPC can be used, probably just splash gear. In another scenario in which the same chemical is released, but is in a tank which is located above your head and you are operating below the tank, then a higher level such as a fully encapsulated suit may be recommended, as full body contact may occur. Use the chemical and physical properties and the task to determine the level of protective clothing required.

Normal Vapor Pressures
14.7 psi
1 atm
760 mm/Hg

Fig. 1
Normal vapour pressure

Volatility is another term that is used sometimes in conjunction with vapour pressure. It means the ability of something to evaporate. The military uses volatility to describe the chemical property of warfare agents. They also use the term *persistency*, which is a combination of vapour pressure and volatility. If an agent is persistent, then once released, it will remain in place for a long period of time. If an agent is non-persistent, it will evaporate or dissipate quickly. There is no period of time associated with this term, but they generally are described in periods of days. Some comparisons are presented in Table 2.

Table 2 **Persistency of some chemical agents**

Agent	Persistency
Sarin	Non-persistent
Soman	Semi-persistent
Tabun	Semi-persistent
VX	Persistent
Mustard	Persistent
Lewisite	Persistent
Hydrogen cyanide	Non-persistent
Cyanogen chloride	Non-persistent

For various materials the vapour pressures as well as their associated volatility is presented in Table 3. Very few information sources list volatility for chemicals, but it is available in some older or more scientific sources. As can be seen in the chart, volatility follows the vapour pressure. There is one other item that impacts the volatility of a substance and that is related to the type of bond that the molecule has. However, in most cases the vapour pressure/volatility relates to the material's ability to vaporize and cause harm. One important note is that most vapour pressures are measured at 20°C (70°F), and if the measurement temperature differs for a particular chemical, then the specific temperature is listed.

The vapour pressures listed in Table 3 run from a very low or, for our purposes, no vapour pressure to some that is considerably higher. This leads us to the discussion of normal vapour pressure or at what point a substance becomes a vapour risk. That point is considered to be 40 *mm/Hg*, according to the scientific community; at that point chemicals begin to evaporate. Some use 20 *mm/Hg* but water has a vapour pressure of 25 *mm/Hg*. For emergency response purposes, that value may be too low. Consider a glass of water (8 ounces) set out on a table. It will take several days for the water to evaporate. Set out the same sized glass of gasoline, and that same

Table 3 **Vapour pressure and volatility**

Chemical	Vapour pressure	Volatility
3 Ethion	0.0000015 mm of mercury @ 21°C	0.031 mg/m^3 @ 20°C
V-Agent	0.0007 mm of mercury @ 21°C	10.5 mg/m^3 @ 25°C
Sulphuric acid	1 mm of mercury @ 145°C	5,362 mg/m^3 @ 145°C
Sodium hydroxide	1 mm of mercury @ 739°C	2,187 mg/m^3 @ 739°C
Fuel oil #2	2 mm of mercury @ 21°C	20,229 mg/m^3 at 20°C
Sarin	2.1 mm of mercury @ 21°C	16,090 mg/m^3 @ 20°C
Xylene	6.72 mm of mercury @ 21°C	39,012 mg/m^3 @ 21°C
Water	25 mm of mercury @ 21°C	22,933 mg/m^3 25°C
Toluene	36.7 mm of mercury @ 21°C	184,908 mg/m^3 @ 20°C
Nitric acid, fuming	62 mm of mercury @ 21°C	213,631 mg/m^3 @ 20°C
Acetone	180 mm of mercury @ 21°C	571,760 mg/m^3 20°C
Gasoline	300 mm of mercury @ 21°C	1,246,607 mg/m^3 20°C
Hydrofluoric acid	400 mm of mercury @ 21°C	437,624 mg/m^3 @ 2.5°C
Ethyl ether	440 mm of mercury @ 21°C	1,783,611 mg/ m^3 20°C

amount will evaporate in a couple of hours. A similar glass of ether will evaporate in a few minutes.

Once a material is known to have a vapour pressure that creates a risk, the next most important factor that affects a material's ability to evaporate is the temperature. The higher the temperature, the more readily the material will create vapours. According to the chart, temperature does play a factor, as most of the listings are for 20 or 25°C. To create 1 *mm/Hg* of vapour, sodium hydroxide must be heated to 739°C. In reality, we could not exist in an environment at that temperature. Even at that point, we would have only 1 *mm/Hg* of vapour being produced.

The vapour pressure is the key to our survival; a material that has a vapour pressure of less than 40 *mm/Hg* presents little risk to the responder as an inhalation hazard. However, it still could present a risk to ingest or touch the material. A release of hydrofluoric acid presents a severe inhalation risk, as it has a high vapour pressure: 400 *mm/Hg* at a very low temperature of 2.5°C, and one can imagine what happens at 70°F (21°C). At that vapour pressure, there is an inhalation, ingestion, and absorption risk. On the other hand, the worst chemical warfare agent has a vapour pressure of 2.1 *mm/Hg*, which is considerably lower than that of water and does not present a vapour hazard.

2.2.6 Vapour density

Vapour density (VD) is the relationship of a given material to the density of air, which is given a value of 1. Materials with a VD of less than 1 will rise in air, whereas materials with a vapour density of greater than 1 will stay low to the ground. The VD is directly related to the molecular weight of the material. The higher the molecular weight, the higher the VD. With one exception (hydrogen cyanide), warfare agents all have VD's greater than 1, so

Table 4 **Vapour densities (air=1) and molecular weight**

Methane	0.55	16	**Phosgene**	3.40	98.90
Ammonia	0.60	17	**Sarin**	4.86	140.11
Hydrogen cyanide	0.93	27	**Mustard**	5.50	192.53
Carbon monoxide	0.96	28	**Tabun**	5.63	162.15
Carbon dioxide	1.53	44	**Soman**	6.33	182.20
Propane	1.56	44	**Lewisite**	7.20	207.31
Cyanogen chloride	2.10	61.5	**VX**	9.20	267.41
Chlorine	2.48	70.9			

will stay low. The higher the VD, the more difficult it is for the material is to rise up and disperse. On the other hand, the higher the VD, the harder it is for the material to escape its container.

2.2.7 Vapour Risk

All things evaporate, but during a chemical accident, it is the rate of evaporation that matters. According to the scientific community, the point at which rapid evaporation occurs is at 40 *mm/Hg*. Some use 25 *mm/Hg* as the rapid evaporation point, since this is the evaporation point for water.

2.3 Classification of HM

The objective is to identify the hazardous properties of chemicals which may constitute a risk during normal handling or use, risks to health, property or the environment.

The user of the chemicals is also to be introduced to the hazards they present and given the basic information, in a suitable manner, such as using a properly made label.

In this document one component chemical is called a substance, a mixture composed of two or more substances is called a preparation. Terms such as “hazardous chemicals”, “hazardous materials”, “chemical agents” or “hazardous agents” and abbreviations HM, HAZMAT, HC will have the same meaning.

The hazards of preparations can be assessed using the information on the hazards presented by their component substances.

For classification purposes the degree of hazard depends not only on the properties of a dangerous substance but also on the level of exposure. This refers to the concentration of hazardous components in the mixtures. In order to assess a preparation it is essential to know also the quantities of its hazardous minor components.

The **EC** and **UN** classification and labelling systems used here as an example can be applied to dangerous substances and preparations. However, these systems should not be applied to medical or veterinary products, cosmetics, munitions or explosives, pesticides specified elsewhere, waste and foodstuffs or animal feedstuffs in the finished stage. These have their own specifications and requirements for labelling.

2.3.1 EC Classification, marking and labelling

Classification

The following properties contribute to risk to health resulting from acute, repeated or prolonged exposure:

- very toxic or toxic
- harmful
- corrosive
- irritant
- cancer causing
- hazards to reproduction
- can cause non-inheritable birth defects
- sensitising

Fire and explosion hazards may be classified as follows:

- explosive
- oxidizing
- extremely flammable
- highly flammable
- flammable

The following properties present a hazard to the environment:

- toxic to living organisms
- persistent in the environment
- bio-accumulative

Substances and preparations that cannot be classified by using the above system may also be regarded as dangerous if they have properties which are hazardous to health, to living organisms or if they can damage property.

Marking and Labelling

All chemicals, both substances and preparations, should be clearly marked to indicate their identity.

Packages and containers of dangerous substances and preparations should, in addition to marking only, have a label with the required information.

The label should draw attention to the inherent danger to persons handling or using the chemical.

Symbols and pictograms have been established for each hazard category listed above. The symbol forms an integral part of the label and gives an immediate idea of the types of hazards that the substance or the preparation may cause.

To specify the type of danger, pertinent standard risk phrases should also be included on the label.

Advices on the precautions necessary in the handling of chemicals are given with standard safety phrases also included on the label.

The chemical supplier, manufacturer or importer, should be able to provide detailed information and a Safety Data Sheet.

In certain countries, such as those of the EU, the manufacturer or importer has the obligation to find and give adequate information about a chemical for assessment of the health and environmental hazards of his chemical for handling and for its labelling.

Safety Data Sheets have been prepared on many dangerous substances and preparations by manufacturers. These should go together with the product to the occupational user. Such information is not always validated or checked.

For information pure substances, International Chemical Safety Cards are available. These contain validated basic information, which may also be used for preparing Safety Data Sheets on the chemical preparations or products.

Lists of classified chemicals exist in several national legislations and regulations which provide information on local requirements in the handling of dangerous chemicals.

Information for classification, and labels, may be obtained from tests, from literature, from practical experience and from information requirements by international rules on the transport of dangerous substances and wastes.

The label is the basic tool to keep the user informed on classification and the most important safety precautions to be taken.

This information must be given if the preparation contains at least one substance classified as dangerous to man or the environment or if the preparation is otherwise regarded as dangerous, for example, flammable, explosive.

In EU countries the label must clearly show

- the trade name
- the name and the address, including telephone number, of the manufacturer, the importer or the distributor
- the chemical name of the substance (in the case of a preparation, the chemical names of the hazardous components)
- danger symbols
- risk phrases (R-phrases)
- safety phrases (S-phrases)
- the quantity of the contents of the package or container

The labels should be in the national, official language(s).

The label should show the chemical names of substances that are primarily responsible for the hazards. As a general rule, a maximum of four chemical names on the label should be sufficient.

In some cases, more than four names may be necessary; for example, all cancer-causing substances in the preparation must be identified and the corresponding R- (Annex 5) and S-phrases (Annex 4) presented on the label.

If the preparation contains one or more of the substances requiring the following R-phrases, both the name of the substance and the R-phrase should be mentioned in the label: R39, R40, R42, R43, R42/43, R45, R46, R47, R48, R49, R60, R61, R62, R63, R64.

As a general rule a maximum of four R-phrases and four S-phrases should suffice to describe the risks and to formulate the most appropriate safety advice.

Symbols showing the most serious hazards should be chosen where more than one danger symbol has to be assigned. As a general rule a maximum of two danger symbols are used.

The explanation of the letter symbols appearing in the attached lists is presented in Table 5.

When more than one danger symbol is used

- the obligation to apply symbol T or T+ will make symbols C, Xn and Xi optional
- the obligation to apply symbol C will make symbols Xn and Xi optional
- the obligation to apply symbol E will make symbols F and O optional

If a preparation is classified both harmful Xn and irritant Xi, it will be labelled harmful Xn, and the irritant properties should be pointed out with appropriate R-phrases. The total amount of the substance in the preparation has an effect in choosing the danger symbols, R- and S-phrases.

Table 5 **Letter symbols and hazardous material class**

Letter symbol	Explanation
E	Explosive
O	Oxidizing
F	Highly Flammable
F+	Extremely Flammable
T	Toxic
T+	Very Toxic
C	Corrosive
Xn	Harmful (less than T)
Xi	Irritant (less than C)
N	Dangerous to the environment

Generally, no account needs to be taken of substances if they are present in following amounts, unless another lower limit has been specifically given:

- less than 0.1% by weight for substances classified as very toxic T+, or toxic T
- less than 1% for substances classified as harmful Xn, corrosive C, irritant Xi

Information such as “non-toxic”, “not harmful” should not be used in the labels.

The pictorial symbol indicating danger is drawn in black and the background colour should be orange.

Classification of a substance - An example

1,1,1 - Trichloroethane, used as solvent
Classified as harmful Xn and dangerous to the environment N, with following R- and S-phrases

R 20	Harmful by inhalation.
R 59	Dangerous for the ozone layer.
S 2	Keep out of the reach of children.
S 24/25	Avoid contact with skin and eyes.
S 59	Refer to manufacturer/supplier for information on recovery/recycling.
S 61	Avoid release to the environment. Refer to special instructions/Safety Data Sheets.

The label should carry this information. Check that the impurities do not exceed the limit of notice for impurity substances classified toxic.

Classification of a preparation - An example

A preparation used for degreasing metal parts, contains following dangerous components

Dangerous substance	%	Symbol	Risk phrases	Safety phrases
Petroleum distillate (flash point 43 °C)	35	T	R45	S53-45
1,1,1 - Trichloroethane	20	Xn, N	R20-59	S24/25-59-61
Xylene (flash point over 21 °C)	12	Xn	R10-20/21-38	S25
Preparation		T, N	R45-10-20/21-59	S53-45-59-61

The R and S-phrases corresponding to the number codes are:

R 10	Flammable.
R 20	Harmful by inhalation.
R 20/21	Harmful by inhalation and in contact with skin.
R 38	Irritating to skin.
R 59	Dangerous for the ozone layer.
S 24/25	Avoid contact with skin and eyes.
S 25	Avoid contact with eyes.
S 45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S 53	Avoid exposure-obtain special instructions before use.
S 59	Refer to manufacturer/supplier for information on recovery/recycling.
S 61	Avoid release to the environment. Refer to special instructions/Safety Data Sheets.

2.3.2 UN Classification

The United Nations has published a book collecting the work of the Committee of Experts: *Recommendations on the Transport of Dangerous Goods*. These recommendations aim to present a basic, practical scheme of provisions that will allow national and international regulations governing various modes of transport to develop within it in a uniform way. The aim is to enable effective and successive transport and to ensure the safety of people, property, and the environment.

In these recommendations the goods are given an identification number and are divided into nine classes describing the inherent hazards (Table 6).

The properties of the chemical substance or product have an effect on the choice of the packing material. Recommendations on the material, as well as the sizes, of packages are based on testing and experience. Dangerous goods of classes 3, 4, 5.1, 6.1, 8, and 9 (Table 6) have been divided for packing purposes into three groups according to the degree of danger they present (Table 7).

Table 6 **UN Classification of hazardous materials (HAZMATs)**

1.	**CLASS EXPLOSIVES**
1.1.	Explosives with a mass explosion hazard
1.2.	Explosives with a projection hazard
1.3.	Explosives with predominantly a fire hazard
1.4.	Explosives with no significant blast hazard
1.5.	Very insensitive explosives; blasting agents
1.6.	Extremely insensitive detonating articles
2.	**GASES**
2.1.	Flammable gases
2.2.	Non-flammable, non-toxic gases
2.3.	Toxic gases
3.	**FLAMMABLE LIQUIDS**
4.	**FLAMMABLE SOLIDS**
4.1.	Flammable solids
4.2.	Substances liable to spontaneous combustion
4.3.	Substances, which in contact with water emit flammable gases
5.	**OXIDIZING SUBSTANCES; ORGANIC PEROXIDES**
5.1.	Oxidising substances
5.2.	Organic peroxides
6.	**POISONOUS (TOXIC) SUBSTANCES**
6.1.	Toxic substances
6.2.	Infectious substances
7.	**RADIOACTIVE MATERIAL**
8.	**CORROSIVE SUBSTANCES**
9.	**MISCELLANEOUS DANGEROUS SUBSTANCES**

Table 7 **Degree of danger and packing groups**

Great danger	Packing Group I
Medium danger	Packing Group II
Minor danger	Packing Group III

The packing group related to a special substance, together with advice on packing methods, is listed in *UN Recommendations on the Transport of Dangerous Goods* and in many national provisions.

To deal with goods having multiple risks a *"subsidiary risk"* classification is used together with the principal hazard classification.

Substances and articles belonging to classes 1, 2, 4.1, 4.2, 4.3, 5.2, 6.2 and 7 often have more than one hazardous property and are subject to further restrictions.

These goods may be:

- explosive
- liable to spontaneous ignition or combustion
- liberate flammable gases on contact with water
- contain infectious micro-organisms that are known or reasonably believed to cause disease in animals or humans
- radioactive
- compressed, condensed or pressurized dissolved gases
- organic peroxides

Examples of hazard classes - Substance or article hazards

UN number	Name and description	Class	Subsidiary risk
3017	Organophosphorus pesticides, liquid, flammable, flash-point not less than 23°C (Demeton, Fenthion, Parathion)	6.1	3
1396	Aluminium powder, uncoated	4.3	
1005	Ammonia, solution with water, with more than 50% ammonia	2.3	8
1789	Hydrochloric acid, solution	8	
1011	Butane	2.1	

2.4 Explosives

2.4.1 Definitions

Explosives are defined as materials capable of violent decomposition. This decomposition often takes the form of extremely rapid oxidation (burning). Explosions result from the sudden and violent release of gas during the decomposition of explosive substances. High temperature, strong shock, and loud noise follow this release.

Explosives are commonly classified as high or low according to the speed of their decomposition. When high explosives are initiated, the reaction is propagated through the filler material at a speed at or above 3,300 feet per second (fps) (1 km/s). These explosives are designed to detonate and destroy a target by a shattering effect. When low explosives are initiated, the reaction is propagated through the filler material at a speed below 3,300 fps. These explosives are designed to deflagrate, or burn rapidly, and destroy a target by a pushing and pulling effect.

After the initial positive pressure phase, a vacuum is created at the explosion site. This creates a negative pressure that moves toward the original centre of the detonation at hurricane speed. It is less sudden, but lasts approximately three times as long as the positive pressure wave.

Fragmentation occurs when the explosive device propels fragments at high speed for long distances. This often accounts for many of the injuries or casualties.

Thermal effects sometimes are referred to as incendiary effects. Heat produced by the detonation of either high or low explosives varies according to the ingredient materials. High explosives generate greater temperatures than low explosives, but the thermal effects from low explosives last longer than those of high explosives.

The thermal effect is visible in the bright flash or fireball temporarily produced by an explosion. Thermal effects vary with the type of explosive, container, addition of fuels/accelerants, shielding, and proximity. Fire and thermal effects are usually localised and short-lived with conventional devices-those not enhanced for collateral incendiary effects.

Table 8 **The EC Classification of explosive substances**

E	Explosive
	This symbol with the word 'explosive' denotes a substance which may explode under the effect of a flame or if subjected to shocks or friction.

2.4.2 EC Classification

The EC Classification denotes explosive substances as presented in Table 8.

2.4.3 UN Classification

Class 1: Explosives

1.1 - Substances and articles that have a mass explosion hazard
1.2 - Substances and articles that have a projection hazard but not a mass explosion hazard
1.3 - Substances and articles that have a fire hazard and either a minor blast hazard or a minor projection hazard but not a mass explosion hazard
1.4 - Substances and articles that present no significant hazard
1.5 - Very insensitive substances that have a mass explosion hazard
1.6 - Extremely insensitive articles, which do not have a mass explosion hazard

This class contains articles, preparations, and substances such as ammunition, TNT, dynamite, nitrourea, fireworks.

Risks involved

An industrial or transport accident involves acute risk of explosion. The pressure wave can be devastating and flying splinters may cause great damage.

The heat of the blast can result in a fire.

Some substances in this class have toxic properties, for example, nitro-glycerine (in dynamite) is also classified as toxic and can penetrate through the skin.

Transport and storage of Class 1 articles or substances are subject to many restrictions, including quantity and temperature limits. They may also be incompatible with other goods. For example, dynamite should not be transported with detonators.

2.5 Flammable substances

2.5.1 EC Classification

The EC Classification of flammable substances is detailed in Table 9.

Table 9 **EC Classification of flamable substances**

F	Highly flammable
	This symbol with the words 'highly flammable' denotes a substance which may become hot and finally catch fire in contact with air at ambient temperature or is a solid and may readily catch fire after brief contact with the source of ignition and which continues to burn/to be consumed by chemical reaction after removal of the source of ignition. If it is a gas it may burn in air at normal pressure. If it were a liquid it would catch fire with slight warming and exposure to a flame. In contact with water or damp air, the substance may release highly flammable gases in dangerous quantities.
F+	Extremely flammable
	The same flammable symbol as above with words 'extremely flammable' denotes, for example, a liquid which would boil at body temperature and would catch fire if vapours are exposed to a flame.

2.5.2 UN Classification

Class 2: Gases

Close to or between explosive and flammable materials are gases that can be explosive and flammable (see above). Some gaseous substances (compressed or liquefied) even though not an explosive, may explode under special conditions.

Under the UN Classification this class contains:

- compressed gases
- liquefied gases
- refrigerated liquefied gases
- compressed gases, which, when packed for transport, are dissolved into a solvent

The term “compressed” refers to gases under pressure but not in a liquid state. Gases are usually stored in cylinders. When the valve is opened or broken, gas alone is released. The pressure of the cylinder depends on the type of gas it contains. The cylinders should always be kept within the approved temperature range to avoid a risk of overpressure causing an explosion hazard. Nitrogen (Class 2.2), hydrogen (2.1), oxygen (2.2 and 5.1) and helium (2.2) are compressed gases.

Condensed gases are in a liquid state at a relative low pressure. The contents are released as liquids which quickly evaporate, forming gas clouds. The size of the cloud can be considerable; for example, 1 litre of liquefied petroleum gas (LPG) forms up to 250 litres of gas.

LPG, (propane, butane or a mixture of them, `cooking gas’) (Class 2.1); propane (2.1); vinyl chloride (2.1); freons; carbon dioxide (2.2); chlorine (2.3 and 5.1); ammonia (2.3 and 8) are commonly used gases in industry and are transported as condensed gases.

Some condensed gases are stored at very low temperatures. They are transported in well-isolated containers called “dewars”. These must have a loosely covered opening to avoid dangerous overpressure. They pose special hazards due to their low temperature. For example, splashes of liquefied nitrogen can cause frostbite and the gas cloud is an asphyxiate.

In a train accident, several tank wagons filled with liquefied propane over turned, spilling their contents. The propane started to evaporate cooling the surroundings to -43°C, which is the boiling temperature of propane. Several persons in the spill area were frozen to death. Due to good luck and tight security, the highly flammable propane gas did not explode.

An example of a dissolved gas is acetylene (Class 2.1). Acetylene cylinders are filled with inert very porous, non-combustible material which is wetted with acetylene.

Aerosols and small receptacles which contain flammable propellant gases belong to this class.

Risks involved

Substances in Class 2 are assigned to one of three categories based on the primary hazard of the gas.

Class 2.1: Flammable gases

This category includes those gases that at normal pressure and temperature, as a mixture of 13% or less with air, can ignite from a source of fire such as a spark.

Class 2.2: Non-flammable, non-toxic gases

Included in this category are gases which might replace oxygen and are an asphyxiate (nitrogen, carbon dioxide), or which are oxidising and may contribute to the combustion of other materials more than air (pure oxygen is an example).

Class 2.3: Toxic gases

Gases which are known to be poisonous or corrosive enough to pose a health hazard belong to this category (carbon monoxide, ethylene oxide, hydrogen sulphide, sulphur dioxide and ammonia).

Containers with toxic gases should never be loaded or stored together with food or feedstuffs.

Acidic gases can react with alkaline gases to produce heat and smoke, which may create a fire risk.

Some gases have more than one dangerous property. They can be both flammable and toxic (methyl ether) or corrosive and toxic (hydrogen chloride, phosgene, chlorine).

Classes 3: Flammable liquids

A flammable liquid has the ability to give off, at normal temperatures, vapours which are flammable (such as, benzene, kerosene, toluene, propanol and various organic solvents used in pesticides). This class also covers mixtures of liquids, as well as liquids containing solids in solution or suspension (paints, varnishes, lacquers, etc.). Petroleum products and crude oil also belong to Class 3.

Risks involved

Flammable liquids pose a risk of fire and explosion, and may lead to expensive environmental clean- up operations (accidents at sea to oil tankers).

The flammability of a liquid depends on several characteristic properties.

The flash-point describes the lowest temperature at which a liquid gives off a sufficient amount of flammable gas to form a mixture with the air which will ignite when a flame or spark is present. If the flash-point is tested to be not more than 60.5°C, the substance belongs to Class 3.

Many flammable liquids can be charged with static electricity, for example, as the result of flowing in a pipe. This makes them both combustible and able to create a spark. Containers should have an earth connection in situations such as refilling cisterns at petrol stations.

Some flammable liquids have more than one dangerous property. Carbon disulphide is both flammable and toxic, and formaldehyde solutions can be both flammable and corrosive.

Class 4.1: Flammable solids

The class 4.1 consists of solids which are readily combustible, those that may cause or contribute to fire through friction, and self-reactive substances. Sulphur, red phosphorus and nitrocellulose films are common hazardous substances in this class. Examples of self-reactive compounds are azocarbamides, benzene sulphohydrazine and diazonium salts. Sawdust, hay and paper are not spontaneously flammable but are in this class because of incompatibility requirements in loading procedures.

Risks involved

When flammable solids are handled there is a possibility of large amounts of dust being released in the air. These mixtures of dust and air can lead to a dust explosion.

Many flammable solids give off hazardous fumes when they are burned. For example, the fumes of burning sulphur or red phosphorous are toxic and corrosive.

The decomposition of self-reactive substances can be initiated by heat, contact with catalytic impurities (acids, bases, heavy metal compounds), friction or impact. Decomposition may result in the emission of toxic gases and vapours. In order to ensure safety during transport, a self-reactive substance may be desensitised using a diluting agent compatible with the substance.

Class 4.2: Substances liable to spontaneous combustion

Linseed oil (used in paints), copra, oily cotton waste, carbon and white phosphorus are examples of substances which can ignite spontaneously when in contact with air.

Risks involved

These substances are liable to act as a source of ignition for other goods and storage structures.

For example, there is a danger of fire if linseed oil spillages are wiped away with rags which then are left to dry in the air. The rags can stay inactive for days before they actually ignite.

Class 4.3: Substances which when in contact with water emit flammable gases

Carbides are among the substances in Class 4.3. Adding water to calcium carbide produces an extremely flammable gas, acetylene. When sodium comes into contact with water it gives off hydrogen gas. The reaction is violent and produces enough heat to ignite hydrogen. Hydrogen burns explosively with such a hot flame that metallic material can start to burn.

Aluminium and magnesium powders, zinc dust and some metal hydrides are in this class.

Risks involved

In addition to the dangers of fire and explosion, goods belonging to this class can react with moisture on human skin and cause burns.

2.6 Oxidizing substances other than organic peroxides

2.6.1 EC Classification

The EC Classification denotes an oxidizing substances or preparations as presented in Table 10.

Table 10 **EC Classification of oxidizing substances other than organic peroxides**

0	Oxidizing
	The symbol with the word 'oxidizing' refers to a substance which releases a lot of heat while it reacts with other substances, particularly flammable substances.

2.6.2 UN Classification

Class 5.1 Oxidizing substances

In this class are substances such as chlorates, chlorites, nitrates, nitrites, chromic acid and concentrated hydrogen peroxide solution.

Risks involved

These goods should be carefully handled and protected from heat or friction. An oxidizing substance has oxygen bound into its structure. This is liberated by heating and can react with other materials or provoke fire.

Many substances in this class are sensitive to impurities. Concentrated hydrogen peroxide solution begins to decompose if a few rust flakes happen to fall into the container. The reaction starts slowly but accelerates with time. It gives off oxygen which corrodes metallic materials. This can be devastating in transport by rail.

The decomposition of oxidising goods can also involve the liberation of toxic or corrosive gases, such as nitrogen oxides, which can be recognised from their deep brown to yellow brown colour.

2.7 Organic peroxides

2.7.1 EC Classification

The EC Classification denotes organic peroxides such as other oxidising materials

2.7.2 UN Classification

Class 5.2: Organic peroxides

This class covers peroxides of organic compounds. They should never be transported or stored with combustible goods. Special recommendations and provisions apply to some of the peroxides because of their high reactivity. In addition to the hazards of explosive decomposition and fire, they are sensitive to impact or friction. Many peroxides are toxic and some of them can provoke allergic response or damage the eyes.

2.8 Poisonous substances

Poisonous substances are studied by toxicology. Toxicology is the science of adverse effects of chemical substances on living organisms. Living organisms include the algae in the sea, animals and people, all flora and fauna. There are no safe substances, all chemicals can be poisonous and cause injury or death. But they can be used safely: the effect depends on the dose and exposure. It is possible by limiting their to handling and benefit from the properties of chemical substances in an `acceptably safe' way. Toxicological studies aim to assess the adverse effects related to different doses in order to find this `acceptably safe' level.

The work is carried out in two phases: first, by collecting data on the properties of chemicals, results of studies and accidental misuse of chemicals, second, by predicting the effects of chemicals in different situations.

To make relevant predictions there must be information available on:

- the substance and its chemical and physical properties
- the biological system affected
- the effects or response caused by the substance
- the exposure (dose, time, situation)

This information is obtained from laboratory tests with cells, bacteria, animals and from accidents involving the substance.

Large amounts of toxicological information are collected into data bases and data banks.

2.8.1 Exposure

To have an adverse effect, a substance must be able to enter the system. The exposure depends on the amount of substance and the period during which it affects the target, for example, humans, animals or bacteria.

2.8.2 Routes

The major routes through which toxic substances may enter the body under normal working condition are:

➠ inhalation
➠ through the skin
➠ ingestion

For many substances the greatest effects and the most rapid responses occur when the substance is inserted directly into the blood circulation. In toxicological animal experiments the routes of exposure may be:

- Inhalation (breathing in)
- Absorption (through the skin or eyes)
- Ingestion, oral (eating, swallowing)
- Transfer across the placenta to the unborn baby
- Intravenous (injection into the vein)
- Intramuscular (injection into the muscle)
- Subcutaneous (injection under the skin)
- Intraperitoneal (injection inside the membrane that lines the interior wall of the abdomen)

Table 11 **EC Classification of poisonous substances**

T	Toxic
	The symbol with a skull and crossed bones with the word 'toxic' denotes a highly hazardous substance.
T+	Very toxic
	The same symbol as above with the words 'very toxic' is used to label a substance, which, if inhaled or ingested or, if it penetrates the skin, may involve extremely serious immediate or long-term health risks and even death.
C	Corrosive
	The symbol with the word 'corrosive' will be found on a label of a substance which may destroy living tissues on contact with them. Severe burns may result from splashes of such a substance.
Xn	Harmful (less than T)
	The symbol with word 'harmful' denotes substances which may cause health hazards less than toxic. It could refer to other types of risks, for example, to allergic reactions.
Xi	Irritant (less than C)
N	Dangerous to the environment

2.8.3 EC Classification

The EC Classification defines poisonous substances as presented in Table 11.

When more than one danger symbol is used

- the obligation to apply symbol T or T+ will make symbols C, Xn and Xi optional
- the obligation to apply symbol C will make symbols Xn and Xi optional

2.8.4 UN Classification

Class 6.1: Toxic substances

Substances in this class are liable either to cause death or serious injury, or to be harmful when swallowed or inhaled or by skin contact. Toxic substances can be gases, solids or liquids. Toxic gases are listed in Class 2.3.

Examples of substances in this class are cyanides, arsenic compounds, mercury and lead compounds, nicotine, toluidines, chloroform, aniline and organotin compounds.

In order to compare the various risks involved, LD50 (lethal dose to 50%) and LC50 (lethal concentration to 50%) are used to appraise toxic properties. LD50 means the dose, at which half of the animals exposed (in laboratory tests) to the poison die, and LC50 means the concentration which kills 50% of the tested animals after being exposed to the substance, usually by inhalation.

There are agreed limits for the levels of toxicity measured in animal tests, with reference to the route of exposure.

The packing group depends on the amount of the chemical and on the different degrees of health hazard that the chemical poses.

Detailed advice about materials and ways of packing can be found in the United Nations *Recommendations on the Transport of Dangerous Goods* and in national regulations.

2.9 Infectious substances

Class 6.2: Infectious substances

These substances cause infectious diseases when they enter the human body by inhalation or another route of exposure.

Accidents with infectious substances are characterised by the onset of symptoms within hours or days. Typically, there will be no characteristic signatures because infectious agents are usually odourless and colourless. Because of the delayed onset of symptoms in a biological accident, the area affected may be greater due to the movement of infected individuals.

Indicators of a possible biological accident

Unusual numbers of sick or dying people or animals. Any number of symptoms may occur. Casualties may occur hours or days after an accident has occurred. The time required before symptoms are observed is dependent on the agent used.

Unscheduled and unusual spray being disseminated, especially if outdoors during periods of darkness.

Abandoned spray devices. Devices may not always have distinct odours.

Personal safety considerations

When approaching a scene that may involve infectious agents, the most critical consideration is the safety of oneself and other responders. Protective clothing and respiratory protection of an appropriate level of safety must be used. Be aware that the presence and identification of CB agents may not be verifiable, especially in the case of biological agents. The following actions/measures to be considered are applicable to either a chemical or biological accident. The guidance is general in nature, not all-encompassing, and its applicability should be evaluated on a case-by-case basis.

Approach and response strategies. Protect yourself and use a safe approach (minimise any exposure time, maximise the distance between you and the item that is likely to harm you, use cover as protection and wear appropriate personal protective equipment and respiratory protection). Identify and estimate the hazard by using indicators as provided above. Isolate the area and secure the scene; potentially contaminated people should be isolated and decontaminated as soon as possible. In the event of a chemical accident, the fading of chemical odours is not necessarily an indication of reduced vapour concentrations.

Some chemicals deaden the senses giving the false perception that the chemical is no longer present.

Decontamination measures. Emergency responders should follow standard decontamination procedures (flush-strip-flush). Mass casualty decontamination should begin as soon as possible by stripping (all clothing) and flushing (with soap and water). If biological agents are involved or suspected, careful washing and use of a brush are more effective. If chemical agents are suspected, the most important and effective decontamination will be that done within the first one or two minutes. If possible, further decontamination should be performed using a 0.5% hypochlorite solution (1 part household bleach mixed with 9 parts water). If biological agents are suspected, a contact time of 10 to 15 minutes should be allowed before rinsing. The solution can be used on soft tissue wounds, but must not be used in eyes or open wounds of the abdomen, chest, brain, or spine. For further information contact the agencies listed in this guidebook.

2.10 Radioactive substances

UN Classification

Class 7: Radioactive material

Markings

Markings are designed to provide an explanation of the contents of a package by using standard terms and codes.

Labelling

Labels are used to visually indicate the type of hazard contained in a package. Labels rely principally on symbols to indicate the hazard. Although the package required for transporting radioactive material is based on the activity **INSIDE** the package, the label required on the package is based on the radiation hazard **OUTSIDE** the package. Radioactive material is the only hazardous material which has three possible labels, depending on the relative radiation levels external to the package. Also, labels for radioactive material are the only ones which require the shipper to write information on the label. The information is a number called the *Transport Index* (TI), which, in reality, is the highest radiation level at 1 metre from the surface of the package. The three labels are commonly called:

- White I
- Yellow II
- Yellow III

They refer to the colour of the label and the Roman numerals are prominently displayed. A specific label is required if the surface radiation limit and the limit at 1 metre satisfy the requirements presented in Table 12).

Table 12 **Labeling of radioactive materials**

Label	Surface radiation level	Radiation level at 1 metre
White 1	Does not exceed 0.5 mrem/hr	Not applicable
Yellow 2	Does not exceed 50 mrem/hr	Does not exceed 1 mrem/hr
Yellow3	Exceeds 50 mrem/hr OR	Exceeds 1 mrem/hr

Since the TI is the radiation level at 1 metre, it is clear that a White 1 label has no TI. A Yellow 2 must have a TI no greater than 1, and a Yellow 3 may have a TI greater than 1. Referring to the radiation limits in section nine for vehicles, it can be seen that the maximum TI for non-exclusive use vehicles (common carriers) and for exclusive use (contract carriers) open vehicles is 10. The radiation level at 1 metre from the surface of a package can exceed 10 mrem/hr only if the package is transported in an exclusive use (contract carrier) closed vehicle.

Placarding

Placards are just bigger labels which are placed on the outside of the vehicle. Unlike labels, there is only one placard and no information need be written on it (that is, no TI). In fact, a placard on a vehicle is only required if the vehicle is carrying a package bearing a Yellow 3 label or LSA material. If the amount of the material being transported constitutes a highway route controlled quantity, the diamond shaped placard has a black square border surrounding it.

2.11 Corrosive substances

2.11.1 EC Classification

The EC Classification (Table 13) puts corrosive substances amongst poisonous ones taking into account corrosiveness to humans only.

Table 13 **EC Classification of corrosive substances**

C	Corrosive
Xi	Irritant (less than C)

2.11.2 UN Classification

Class 8: Corrosive substances

The corrosive substances class is a large one. It can be subdivided into acids, bases and other materials.

Examples of acids include hydrochloric acid, sulphuric acid and acetic anhydride. Sodium hydroxide, potassium hydroxide, sodium carbonate and sodium metasilicate are bases or alkalis. Other corrosive substances include antimony pentachloride (textile impregnation), titanium tetrachloride, aluminium chloride and hypochlorites.

pH	Description
14	Very alkaline (caustic soda)
13	
12	
11	
10	
9	
8	
7	Neutral (water)
6	
5	
4	
3	
2	
1	Very acidic (nitric acid)

Fig. 2 **pH Scale for determining corrosiveness of substances**

The health hazard varies from corrosive to irritating, depending on the type and concentration of the active substance.

The corrosiveness of the substance is determined by its pH which measures the level of acidity or alkalinity. The scale presented in Fig. 2 shows how the substance can be classified as corrosive or irritant.

The pH value can often be found on the label or in the documents following the substance.

Some countries require that solutions must be classified, because of the corrosive effects, when the pH value is less than 1.5 or greater than 11.5.

The pH of some common substances in dilute water solutions is given in Table 14.

Acids and alkalis are normally transported at very high concentrations; for example: 90 - 95% sulphuric acid, 65% nitric acid, 30% hydrochloric acid, 50% sodium hydroxide and 50% phosphoric acid. At these concentrations the pH value is not important, the substances are simply very corrosive.

Table 14 **The pH of some common substances in dilute water solutions**

Substance	Concentration	Smell	pH	Effect on skin
Hydrochloric acid	1%	sharp	~0.6	Slight feeling
Acetic acid	1%	typical	~2.8	None
Sodium hydroxide (caustic soda)	1%	none	~13.4	Strong
Ammonia	1%	sharp	~11.4	Irritating

Risks involved

These substances can attack and corrode many materials, for example, clothes, paper and several metals. Decomposition often produces heat and gases, and in some cases extremely flammable hydrogen gas. The choice of a packing material and loading should be carefully planned, because it can be some time before the consequences of corrosive effects are visible.

Accidental mixing of different corrosive materials can in some cases lead to violent reactions, which may give off large amounts of gases.

In the case of strong alkalis there is a latent period before a burning feeling on the skin is experienced. By then the damage is already done. Skin contact with strong acids produces an immediate feeling. Both types of corrosive substances can cause serious skin damage.

Corrosive material in the eyes requires a very rapid and long rinse with water (for at least 15 minutes) and medical attention.

Corrosive substances can also present other hazards. For example, benzyl chloride is both toxic and corrosive, and cyclohexylamine is both corrosive and flammable.

2.12 Miscellaneous dangerous substances

UN Classification

Class 9: Miscellaneous dangerous substances

These are substances and articles which during transport present a danger not covered by other classes.

For example, magnetic materials can be classified in this category (magnetism may affect the navigation systems of aeroplanes).

PCBs (polychlorinated biphenyls) are placed in Class 9 because they may damage the environment.

Dry ice (solid carbon dioxide) can evaporate, producing asphyxiant fumes, and displace oxygen in the air in confined places such as cargo holds in ships and storage cellars.

Asbestos can damage the lungs. The effect on health is not immediate; the damage appears after many years. Therefore asbestos is not placed in Class 6.1 but in Class 9.

Concentrated formaldehyde solutions are flammable, but if they are diluted with water the flash-point becomes higher than 60.5°C, which is the limit of flammables. The remaining hazards are still present, such as the allergic reactions caused by formaldehyde.

2.13 HM Sources

Chemicals have become a part of our life, sustaining many of our activities, preventing and controlling many diseases, increasing agricultural productivity.

However one cannot ignore the fact that many of these chemicals may, especially if not properly used, endanger our health and poison our environment.

It has been estimated that approximately one thousand new chemicals come onto the market every year, and about 100 000 chemical substances are used on a global scale. These chemicals are usually found as mixtures in commercial products. One to two million such products or trade names exist in most industrialised countries.

More substances and rising production mean more storage, transport, handling, use and disposal of chemicals. The whole life cycle of a chemical should be considered when assessing its dangers and benefits.

Most chemical accidents have a limited effect. Occasionally there is a disaster like the one in Bhopal, India, in 1984, with thousands of deaths and many people permanently disabled.

It is not just the worker handling chemicals who is at risk. We may be exposed in our homes through misuse or by accidents, and be contaminated by consumer products, including food.

The environment may be affected; chemicals may pollute the air we breathe, the water we drink, and the food we eat. They may have entered into forests and lakes, destroying wildlife and changing the ecosystems.

All chemicals are not of equal concern. The assessment of the health risks of chemical substances is a continuous process in which information on the chemical hazards is made available through a variety of sources.

Remember: chemicals have power, and that is why they have become an important part of our life. Respect that power and handle them with care.

Common chemical groups that cause health risks

Dusts, fumes and gases

Dust may be just a nuisance. The danger depends on the type of material in the dust and on the amount and the size of the particles.

The smaller the particle is, the deeper it will penetrate into the lungs with inhaled air, thereby passing through the defensive systems of the lungs. This type of dust is invisible to the eye and can be identified using a microscope. Such dust can accumulate in the lungs over a long period of time and cause a lung disease called pneumoconiosis, a common, incapacitating, occupational disease. Dusts containing crystalline silica or asbestos most frequently can cause this condition.

Sand and many types of stone contain crystalline silica, as do many ores, concrete, ceramics and diatomite. Processing of these materials creates dust with the result of silica accumulating in the lungs. After many years this may lead to an incurable lung disease, even though exposure ended many years before.

Asbestos is a natural mineral fibre which is very resistant to fire and to many chemicals. Asbestos fibres are very strong and thin. Asbestos exists in various forms and names: chrysotile, crocidolite, amosite, antophyllite, actinolite and tremolite asbestos. Chrysotile is used in isolating materials, protective carpets and clothes.

The dust containing asbestos particles penetrates the lungs, destroying the lung tissue. This condition is called asbestosis. Asbestos can also cause lung cancer. The risk of cancer is many times higher if the asbestos exposure is combined with smoking. Many countries have restricted or banned the use of asbestos.

Exposure to metal fumes can cause damage to the body. `Metal fume fever' is a known health effect when metal fumes, often containing zinc, are inhaled. It usually appears on the day following that of the exposure.

Gases do not necessarily have a warning odour in a dangerous concentration. The odour may be apparent only when there is a very high concentration in the air. Gases may have an irritating effect, or they may enter the blood circulation and cause internal damage.

Sulphur oxides, nitrogen oxides, chlorine and ammonia are toxic gases that are corrosive and irritating to the respiratory system. They are widely used in industry. Phosgene is formed when solvents containing chlorine, such as "TRI" (1,1,2-trichloroethylene), come into contact with hot surfaces or flames. Phosgene can be deadly poisonous even before the odour is detected.

Carbon monoxide is a toxic, odourless, colourless gas which is formed by the incomplete burning of materials of organic origin. It may enter the blood circulation. Some gases can pass through the skin, as, for example, hydrogen cyanide.

Solvents

Most solvents are liquid organic chemicals. They are used because of their ability to dissolve other substances, particularly fat and grease, which are insoluble in water. Many of them evaporate rapidly at ambient temperatures. They are often flammable and may ignite by heat from smoking, welding or static electricity. Vapours move with air currents and can ignite even by means of a distant heat source.

Inhalation is the most common way for solvents to enter the body, but some of them penetrate intact, healthy skin. Once in the blood stream, a solvent can be transported to different organs, such as the brain and liver.

Solvents have different effects on humans, depending on their evaporation rate and their solubility in water. The risks to health depend on the period of exposure and the concentration of the solvent in the inhaled air.

Many solvents have a narcotic effect; they may cause dizziness, headache, reduced comprehension or tiredness. They may also irritate the eyes and the respiratory tract. Frequent skin contact attacks the protective layer of the skin, causing irritation. Some solvents are very hazardous to the liver, kidneys, bone marrow or nervous system. Benzene, carbon tetrachloride and carbon disulphide belong to the category of solvents which should be substituted with less dangerous ones.

The main sources of HM listed bellow are:

- Industry and HM production especially
- HM storage
- HM transportation
- HM disposal and utilisation

2.14 HM production

Development of emission scenarios for chemicals is a critical part of environmental exposure assessment. However, gathering information on the uses and releases of industrial chemicals is not an easy task and is sometimes very time consuming and costly.

This list of categories of HM industries has been designed to provide readily accessible information on the uses and releases of industrial chemicals for exposure/risk assessors. It is also expected that this database will help to avoid duplication of work on the development of default emissions scenarios.

The "industry category" comprises 16, while the "use category" comprises 56 categories, as presented in Tables 15 and 16, respectively.

Table 15 **"Industry category" of hazardous materials**

1)	Agricultural industry (for example, pesticides, fertilisers)
2)	Basic chemical industry (basic chemicals for example, Solvents, pH-regulating agents (acids, alkalis))
3)	Chemical industry (chemicals used in synthesis for example, intermediates (including monomers), process regulators)
4)	Electrical/electronic engineering industry (for example, electrolytes, semiconductors. But: galvanics, electroplating agents)
5)	Fuel industry (for example, gasoline, colouring agents, fuel additives, anti-knock agents)
6)	Leather processing industry (for example, dyestuffs, tanning auxiliaries)
7)	Metal extraction, refining and processing industry (for example, heat transferring agents, electroplating agents)
8)	Paints, lacquers and varnishes industry (for example, solvents, viscosity adjusters, dyestuffs)
9)	Paper, pulp and board industry (for example, dyestuffs, toners)
10)	Personal and domestic use (for example, consumer products such as detergents (including additives), cosmetics, non-agricultural pesticides for domestic use)
11)	Photographic industry (for example, antifogging agents, sensitisers)
12)	Polymers industry (for example, stabilisers, softeners, antistatic agents, dyestuffs)
13)	Public domain (for example, professional products used in public areas such as non-agricultural pesticides, cleaning agents)
14)	Textile processing industry (for example, dyestuffs, flame retardants)
15)	Other
16)	Unclassified

2.15 HM Storage

Ideally, hazardous materials must be stored separately from other material. This may be accomplished by:

- separate storage buildings or compounds
- separate storage compartments separated by fire walls and fire doors
- separation by hazard classes with the appropriate fire safety distances, and the installation of fixed automatic fire extinguishing systems in compartments or the entire building

Table 16 **"Use category" of hazardous materials**

1) Absorbents and adsorbents
2) Adhesive, binding agents
3) Aerosol propellants
4) Anti-condensation agents
5) Anti-freezing agents
6) Anti-set-off and anti-adhesive agents
7) Anti-static agents
8) Bleaching agents
9) Cleaning/washing agents and disinfectants
10) Colouring agents
11) Complexing agents
12) Conductive agents
13) Construction materials additives
14) Corrosion inhibitors
15) Cosmetics
16) Dust binding agents
17) Electroplating agents
18) Explosives
19) Fertilisers
20) Fillers
21) Fixing agents
22) Flame retardants and fire preventing agents
23) Flotation agents
24) Flux agents for casting
25) Foaming agents
26) Food/foodstuff additives
27) Fuel
28) Fuel additives
29) Heat transferring agents
30) Hydraulic fluids and additives
31) Impregnation agents
32) Insulating materials
33) Intermediates
34) Laboratory chemicals
35) Lubricants and additives
36) Non-agricultural pesticides
37) Odour agents
38) Oxidising agents
39) pH-regulating agents
40) Pesticides
41) Pharmaceuticals
42) Photochemicals
43) Process regulators
44) Reducing agents
45) Reprographic agents
46) Semiconductors
47) Softeners
48) Solvents
49) Stabilisers
50) Surface-active agents
51) Tanning agents
52) Viscosity adjusters
53) Vulcanising agents
54) Welding and soldering agents
55) Others
56) Unclassifieda

2.15.1 Chemical compatibility

The major factor to be considered when storing hazardous materials is chemical compatibility. Incompatible items may chemically react causing serious damage or loss when placed together. For this reason, segregation is absolutely necessary to prevent serious accident. The Hazardous Material General Storage Compatibility Chart may be used for general information purposes, but it is important to refer to the applicable Hazardous Material Guide Sheet (HMGS) for more detailed information prior to storing hazardous materials. These documents, along with the HMGS, are to be consulted whenever two or more chemicals are to be stored in the same approximate location. In instances where the compatibility list, the compatibility chart and the HMGS do not provide the required information, the applicable hazardous materials control regulations or specialist advisors should be consulted.

2.15.2 General safety and hygiene

Worker eating facilities and rest areas must be remote from hazardous materials storage and work areas. Employee change rooms (with separate lockers for street and work clothes) and washrooms should not be located near the dangerous areas. Deluge showers and eyewash stations must be located in the storage and work areas as appropriate.

2.15.3 Inventory importance

Once a hazardous material has been issued by the supply facility, it is important that some record be maintained of its existence until it is returned to the supply facility for disposal. A complete and accurate inventory maintained by users is essential to the effective management of a hazardous material control program. The inventory provides the system upon which users identify hazardous material storage use areas, holding limits are set, employee training is determined and vital emergency response information is obtained and made readily available.

2.15.4 Responsibility

Those managing the workplace are responsible for ensuring that the inventory is complete, accurately maintained and updated as changes occur. The inventory list must be available to all employees, OSH workplace committee members, hazardous material coordination officers, safety officers and emergency response agencies.

2.15.5 Inventory content

The inventory list is to include all hazardous products located in the workplace. These materials shall be stored in accordance with the applicable hazardous control regulations. For example, explosives control should be in accordance with the CFP 153 series of explosive safety manuals. The required regulations include, but are not limited to, federal publications, Canadian Forces Policies and manufacturers' instructions.

2.15.6 Inspections and surveys

In order that storage areas are maintained to a level which ensures the safety and well-being of users and occupants, properly planned and executed inspection and survey procedures must be implemented and followed. These procedures are established to detect existing defects in procedures, practices and equipment, and assist in preventing injury, occupational illness, damage or loss. Inventory inspection offers the most positive and constructive technique for implementing preventive action in the control and management of hazardous material holdings, rather than post-accident curative action.

A properly organised hazardous materials inspection system should be integrated within the broader aspects of general safety inspections and surveys. In this chapter the reader has had the opportunity to learn about detecting and reducing hazards encountered in the storage of hazardous materials, and in producing an inventory for stored hazardous materials.

2.15.7 Special consideration

All personnel should ensure that:

- Hazardous materials are stored to prevent exposure to direct sunlight or located heat
- Incompatible materials are stored by hazard class

Storing and handling of some hazardous substances

Acids

Large bottles of acid should be stored on a low shelf or in approved cabinets

Oxidizing acids should be segregated form organic acids, flammable and combustible materials

Acids should be kept separate from bases and alkaline metals such as sodium and potassium

Spill control plans and equipment should be available for acid spills

Bases

Bases are stored away form acids

Solutions of inorganic hydroxides are stored in polyethylene containers

Spill control plans and equipment are available for caustic spills

Oxidisers

Oxidisers are stored away form flammable and combustible materials and reducing agents such as zinc, alkaline metals and formic acid

Water-reactive materials

Materials are kept in a cool, DRY place

A dry chemical fire extinguisher system is used

Flammable

All flammable liquids are kept in approved storage area in approved containers

All electrical service equipment is explosive-proof

Firefighting equipment is readily available

When dispensing flammable liquids into a metal container, a static bonding line is used to connect the drum and

All storage containers larger than gallons are properly grounded to an approved grounding point

Toxic materials

Toxic material, carcinogens and teratogens are kept in a secure area accessible only to authorised personnel

Emergency response actions are posted

Special in-house problems

Identify protective requirements and add to this list

Materials handling equipment (MHE)

- MHE is grounded
- MHE is checked daily for defective operation
- The right type of MHE is being used around hazardous materials
- Moving (electrical) parts are guarded
- Wiring, switches, and fuses are free of defects

Storage areas

- Hazardous storage areas are properly and prominently marked or identified
- Hazardous areas are secured at all times when not in use with access only to authorised personnel
- Emergency response drills are known by all and have been practised

- Information on the incompatibility of materials is available for consultation for safe storage arrangement
- Incompatibility charts should be posted

2.16 HM transportation

What happens during the transport of chemicals?

Industrial production takes place, and raw materials are located, all over the world. Transport is necessary for products to reach consumers. The transport and storage of dangerous chemicals and goods has increased with technical development and production development.

An accident occurring during the transport of dangerous goods can lead to catastrophic consequences; Laws and recommendations have been established to protect society and the environment. But they can not be effective if you, whether you are an employer, worker, transporter or inspecting authority, do not share the responsibility and follow existing recommendations and guidelines of transport and storage in order to avoid unnecessary risks.

The hazardous properties of products or chemicals should be clearly stated so that people at all stages in the transport chain are aware of them. This information should always accompany the goods so that people can recognise the risks, avoid accidental mishandling and have the right kind of the personal protection at their disposal in case of leakage.

Dangerous goods can be transported without causing unnecessary hazards if handled properly and with care.

The empty containers and packages of dangerous goods can present the same hazards as the chemical substance or product they contained and should also be regarded as dangerous goods.

50 per cent of transported goods are dangerous

United Nations statistics show that half of all goods transported belong to the category of dangerous goods. Petroleum products transported by tankers form a large proportion of all transported goods, but road and railway transport is also significant.

For example, 85% of chlorine, which is one of the very dangerous chemicals, is transported by rail.

Large amounts of other highly dangerous goods, such as hydrochloric acid, sulphuric acid, sulphuric dioxide, nitric acid, phenol and methanol are transported regularly.

Small drains make a river

Major accidents cause extensive damage but that is not all. We forget easily that small amounts of oil, gasoline, battery acids and refrigerator fluids are released to environment daily. Even small but frequent wastes from ships, households, cars or agriculture increase the load to the environment. For example one litre of oil can, under unfavourable circumstances, spoil 100 000 litres of drinking water. A spill of hydraulic fluid from a truck can lead to environmental damages.

Recommendations and instructions for the handling, storage and transport of dangerous goods must be clear and unambiguous to avoid harmful or dangerous circumstances.

Under normal conditions, transport of dangerous goods does not pose a greater danger than any other transported goods if the responsible persons in the transport chain respect the existing recommendations and laws and are aware of the type of the hazards of the cargo.

Dangerous situations

There is always a risk of spillage during the transport of hazardous goods. When incompatible substances mix with each other, there is a possibility of a chemical reaction, which can produce enough heat to cause fire or explosion and can release dangerous gases. For example, toxic nitrous oxides are formed when ammonium nitrate (in fertilizers) decomposes in a fire. Another example is the toxic gases which fume off when a spillage of concentrated sulphuric acid is absorbed in sawdust.

Spillages are possible in the following situations:

- goods are not properly packaged
- handling (loading, unloading, etc.) is done without reference to the contents, (perhaps because of missing or incomplete labelling)
- fire, either when the load or the vehicle is burning
- collision or capsize
- defective tightness or incomplete closing of valves and connections

A risk of an accident is present when

- vehicles carrying dangerous goods are left to stand unattended
- the vehicle or container runs loose because it is not properly connected or secured
- the load starts to move during transport
- spillage are not quickly washed away from the vehicles or containers
- spillage are not properly cleaned

Special conditions can increase the risks.

A chemical substance or preparation may be hazardous in itself when it comes into contact with other chemicals including air, water or humidity. For example, when calcium carbide (used in the production of acetylene and pyrotechnics) comes into contact with water, it releases the extremely flammable gas acetylene (used in a welding flame) and creates an explosion hazard.

Careful handling is also important because the magnitude of the involved risk is not always obvious. One kilo of a certain chemical poses a hazard, but it is not obvious that ten kilos create a tenfold hazard. The danger could be the same as for one kilo or it could be higher.

The pressure within sealed packages rises in the heat (sunshine), and can lead to uncontrollable reactions.

Changes in temperatures may affect both the qualities of a cargo and its packing material.

The recommendations on package sizes as well as the load size should be respected.

Common hazards in handling chemicals are

- risk of explosion
- fire and smoke
- chemical health hazards: immediate or delayed poisoning,
- burns, allergies
- damage to the environment

Many companies allow uncontrolled access by diesel engines, believing that they cannot ignite gas or vapour. This is incorrect as presented in enclosed examples.

Frequent types of incidents

Example 1: Four tons of hot, flammable hydrocarbons leaked out of a plant while maintenance work was in process. A diesel engine was running in the area. The flammable vapour was sucked into the air inlet and the engine started to race. The driver tried to stop the engine by stopping the fuel supply (usual way of stopping a diesel engine) but without success as burning material was coming in through the air inlet. Finally there was a flash-back and the flammable liquid ignited to cause a fire.

Example 2: A tank trailer tipped up because the rear compartments were emptied first. If it is not possible to keep a trailer connected to the truck's driving unit, the front compartments should be filled last and emptied first, as the normal support cannot alone prevent the trailer from tipping.

2.16.1 Transport of dangerous goods

Whenever dangerous goods are to be for transported certain measures should be taken to ensure that the potential risks are adequately communicated to all who may come into contact with the goods in the course of the transport. This can be accomplished through marking and labelling of packages to indicate the hazards of the consignment, through including relevant information in the transport documents, and by placing placards on the transport units, both containers and vehicles.

Labels, marking, documents

Each package should be marked with the appropriate shipping name, hazard class and UN number, followed by the packing group reference (when available), for example:

ALLYL ALCOHOL 6.1 UN 1098 I

Labelling is based on the UN classification of dangerous goods into the nine classes described above.

Detailed instructions on how dangerous goods should be classified and packed are given in international agreements and national provisions.

Labels should be placed on containers and vehicles so that they are clearly visible.

During the transport of dangerous general goods, the appropriate warning labels should be on every single package.

Only one danger class label should normally be fixed on a package. However, if the sub-

Primary Subsidiary label	Primary Subsidiary label
Methanol	**Dibenzoyl peroxide**

stance or article presents more than one significant risk, such as fire and poisoning, the package should bear labels indicating important subsidiary risks, for example:

Keep dry	**This side up**	**Fragile**

Special labels indicating the transport conditions are:

The documentation for the transport of dangerous goods should contain:

➠ Transport document containing:
- the appropriate shipping name
- the class and, when assigned, the category in this class of goods
- the UN number and, where assigned, the packing group for the substance
- the total quantity of dangerous goods covered by the document (by volume, mass, or net explosive content, as appropriate)
- the name and address of the consignor and the consignee

In addition:

- Other elements of information deemed necessary by national authorities, such as flash point

If dangerous waste is transported for disposal, the proper shipping name should be preceded by the word “WASTE”

➠ Declaration or certificate that the consignment offered can be accepted for transport, and that the goods are properly packed, marked and labelled

Vehicle requirements

Transport by road may take place as bulk materials, or in containers and tanks.

The detailed technical requirements for different transport methods are usually given in national regulations.

The transporters should check that the following documents are attached:

- transport document (letter of consignment)
- declaration that the packing and labelling is properly done
- transport emergency card (instructions in writing in case of accident or emergency that may occur during transport)
- driver’s training certificate
- certificate of approval given by technical inspection for the tank and vehicle
- labels and placards for the vehicle
- packing certificate of the container

Every transport unit carrying dangerous goods should be equipped with:

- fire-fighting appliances (chosen according to the type of load)
- tool kit for emergency repairs to the vehicle
- at least one scotch (mechanical brake) of a size suitable for the weight of the vehicle and the size of the tyre

- two amber lights independent of the electrical system of the vehicle
- placards, according to the transported goods
- protective equipment (for personal protection, absorbing material for spills, etc.)

Incompatible dangerous goods

Detailed instructions pertaining to classified dangerous goods may also restrict the transport of specific goods together in the same vehicle, or the minimum distances between two such packages may be given.

Those people responsible for loading the goods have to rely on the information found on packages and transport documents. Opening of the transport containers or the packages during transport or intermediate storage is not permitted.

Once the labelling is properly completed, loading personnel can use the attached key symbols to judge how to construct the load according to regulations and in a safe way.

Limited quantities

Dangerous goods require special treatment, equipment, extra vehicle crews and supervision when stored, handled, parked, and at places of loading and unloading.

Detailed instructions in international and national provisions specify quantity limits for certain dangerous substances. These maximum package quantities can be transported in one transport unit, and not all of the above-mentioned special precautions need to be applied.

Such limits are given in the UN Recommendations on the Transport of Dangerous Goods. They are adapted and more detailed in the European Agreement Concerning the Carriage of Dangerous Goods by Road (ADR).

2.16.2 Organizing safety

Safety measures should be considered throughout the transportation process, from the request for transport up to the delivery at the end-point, including the cleaning of the vehicle afterwards.

All levels of personnel involved should be well informed and these people should share the responsibility.

Safety measures should include organisational, personnel and engineering aspects, and co-operation between operational staff during the transport should be emphasised.

Collaboration between the employer and employees is essential. Collaboration with authorities, such as responsible community and health care institutions and labour inspectors is equally important in order to exchange information and plan for emergencies.

Organizing safety communication

Proper communication within the transport chain is the basis for all other safety measures.

Safety activities are targeted to:

- point out practical problems concerning either the workplace as a whole or individual tasks
- create a forum to discuss these problems and to try to find solutions that improve the health of workers and reduce loss of materials
- find out the risks of the work and the effects of these risks and to suggest a solution to minimize them
- establish a priority list of improvements, with respect to time and resources

- ensure that the suggested practical solution are properly implemented and the results are improving the situation
- promote good housekeeping in the working environment

This should involve all parties in the workplace. The task could be given to a committee including representatives of different parts of the transport company.

The committee could consider emergency planning and safety education. Ideas from both workers and the employer should be encouraged and discussed.

Organizing safety measures

Transport order, booking

When accepting a transport order, one should immediately establish whether the batch contains dangerous goods.

If the batch does, or is suspected to contain dangerous goods, the consignor should be reminded of the need to label the goods according to regulations and to prepare documents which include instructions in the local language in case of emergency or spillage.

Some companies have developed checklists of different aspects of information, which the consignor can use to describe the load in order to facilitate the communication between different stages of the transport chain.

If the cargo is transported in a tank-container or as bulk transport, a special check should be made that the vehicle is properly equipped, that proper placards are chosen, that the vehicle and its pipes and connections are empty and clean, and that the protective equipment is intended for those hazards the transported goods can cause (such as provision of the right type of filter for the driver's gas mask).

Loading

Before leaving the loading place, all documents should be checked. Always remove old documents from the vehicle to avoid any misunderstanding in case of an emergency. See that the documents are completed. If passing through customs, check that the emergency instructions are written in the appropriate languages. The packages and containers should not be broken, and the actual amount should be the same as stated in the documents. Dangerous goods should always be well attached to avoid load movements during transport and they should be loaded away from food and animal foodstuffs. Attach the placard to the vehicle.

Remember grounding to avoid static electricity, and personal protective equipment when loading dangerous goods into/from tank containers.

A sketch of the load showing where the dangerous goods are situated could save time in unloading.

Unloading and re-transport

A check should be made that the documents are always attached to the goods. To avoid unnecessary risks intermediate storage should be planned, according to the class to which the goods belong, to avoid contact between incompatible chemicals. A checklist for re-transport helps the workers in the storage area and enhances safety.

Some dangerous goods must be under surveillance at all times, such as explosives, organic peroxides and toluene sulphonic acid. Some other dangerous goods need limited surveillance while parked in a restricted area or isolated place if the amount exceeds specified quantities.

Delivery

You should check that loaded dangerous goods have not moved and that the packages/containers are not leaking. If there is a spillage, follow the cleaning instructions described in the attached documents.

Dangerous goods can be delivered only to the authorised persons and should not be left without surveillance.

Check that the name(s) of the goods and the amounts correspond to those in the documents. In the case of liquids being transported in a tank container, check that connections and pipes are not leaking. Supervise the unloading to avoid an overflow.

Do not forget to give the documents to the receiver of the cargo and remember to remove the placards when they are no longer needed.

Responsibilities

It is the responsibility of the consignor to see that

Common rules for all types of transport of dangerous goods

- **Read the transport document(s) before loading in order to master the loading process and to know what to do in case of an accident or spill**
- **Do not leave the vehicle containing dangerous goods unattended**
- **Loading and unloading of some dangerous goods in public places requires the presence of or notice to authorities (police, customs)**
- **Do not take passenger(s)**
- **Do not smoke during loading operations, close to a vehicle that is waiting to be unloaded, or inside the vehicle**
- **Never use open flames of any kind in the area where there are dangerous or unknown goods. Do not keep engines running when they are not needed for loading (pumping, lifting...)**
- **See that the goods, the names and the amount are the same in reality as in the enclosed documents**
- **See that dangerous goods do not come into contact with food and feedstuff**
- **See that the labels are placed on the dangerous goods and on the vehicle**
- **Separate dangerous goods from other goods that are being transported and place them properly (make a sketch where they are located in the vehicle)**
- **See that the load cannot move during transport (well fixed, no oil on floor that would make it slippery). See that there is available the necessary equipment to conduct (un)loading and transport safely (for example, grounding cables, personal protection equipment)**
- **Do not accept for transport damaged dangerous goods or leaking packages or containers**
- **Drivers have no right to open packages or containers with dangerous goods**

- goods are classified according to national and international regulations
- the limitations on the transport of certain goods are respected
- the goods are properly packed and marked the appropriate documents are attached to the goods

The responsibilities of the transporters are

- to equip the vehicle to meet national and international regulations
- to see that the workers and drivers are trained to transport dangerous goods
- to plan the transport, for example, to select routes avoiding dense residential areas, and to arrange supervision during parking.

The driver of a vehicle is responsible for

- having the necessary documents for the load at hand
- accepting only undamaged, marked or labelled packages and containers
- checking that he is well informed about the transport details
- following the instructions given, such as the use of personal protective equipment, and not undertaking certain tasks alone

2.17 HM utilisation

There have been several instances of major industrial disasters related to the use of chemicals. Although they are individual accidents, different in the way in which they happened and the chemicals that were involved, they have one common feature: they were uncontrolled, involving fires, explosions or the release of toxic substances that either resulted in the death and injury of large numbers of people inside and outside of the factory or caused extensive damage to the property and the environment.

Accidents involving major hazards could start with leakage of a flammable substance, mixing of the substance with air, formation of a flammable vapour cloud and drifting of the cloud to a source of ignition leading to a fire or an explosion.

These clouds would directly affect the site as well as possibly the surrounding populated areas. In the case of flammable substances the greatest danger arises from a sudden massive escape of volatile liquids or gases. If the cloud were ignited, the effects of combustion would depend on many factors, such as wind speed and the extent to which the cloud was diluted. The area affected would generally be limited to a few hundred metres from the site.

Much larger areas can be dangerously affected in a sudden release or by very large quantities of toxic materials. In favourable conditions such a cloud can still contain lethal concentrations of toxic chemicals several kilometres from the accident site. The extent of casualty depends on the number of people in the path of the cloud and on the efficiency of emergency arrangements, for example, evacuation before the cloud reaches the populated areas.

The effect can also migrate into other factories situated nearby and containing flammable, reactive or toxic chemicals, escalating the disaster. This is sometimes referred to as the `domino effect’.

Not only does the cloud itself pose a health hazard. The fires also cause depletion of oxygen and fumes generated by the fire may contain toxic gases.

Chlorine and ammonia are the toxic chemicals most commonly used in quantities large enough to pose a major hazard. Both have a history of major accidents. There are also other chemicals which, although used in smaller quantities, should be handled with particular care because of their higher toxicity.

An industrial accident classified as a `major hazard' leads to tighter control, more specific than that applied in the normal factory operations. This is in order to protect both workers and outside people, to avoid economical losses to the factory and damage to the environment.

The first step in a systematic approach is to identify the installations susceptible to a `major hazard'. For this purpose, the European Union has a Directive which has been in use since 1984. The Directive sets certain criteria based on the toxic, flammable and explosive properties of the chemicals. For the selection of specific industrial activities which involve a `major hazard' risk, a list of substances with limit amounts is provided. The list contains 180 toxic substances with the limits varying from one kilogram for extremely toxic substances to 50, 000 tons for highly flammable liquids.

2.18 HM identification and detection

Air monitoring/liquid sampling is one of the most important activities in the response to chemical accidents and will play an increased role in the response to terrorist accidents. A response team that is not skilled in air monitoring is at an extreme disadvantage and, in most cases, will have to assume that a chemical hazard exists, even if it doesn't. The use of air monitoring and sampling equipment is complicated and requires practice, and when dealing with terrorism agents there will be extreme pressure for quick results. Terrorism agents are a largely unknown field and could be placed in the "once-in-a-lifetime" category. It is not the intention of this section to provide exhaustive information on air monitoring, but to provide the student with an overview of air monitoring and its important role in emergency response. It is important to note that developments in the detection of terrorism agents are occurring every day, and much of this technology looks promising for use in standard HM response.

2.18.1 Meter terminology

To fully comprehend the use of air monitors, the responder first must comprehend the basic terminology that is generic to all monitors. More detailed information related to the specific monitors is provided in later sections.

Accuracy is the ability of the meter to produce findings close to the actual quantity of gas.

Precision is used to describe the ability of the monitor to reproduce the same results each time it samples the same atmosphere; in other words, it duplicates the readings each time the same concentration of gas is sampled.

Table 17 **Gas quantity measurement by meter with different accuracy**

Meter	Known quantity of gas	1st reading	2nd reading	3rd reading	4th reading	Meter description
Meter A	100 ppm	50 ppm	50 ppm	50 ppm	50 ppm	Precise
Meter B	100 ppm	100 ppm	100 ppm	100 ppm	100 ppm	Accurate and precise
Meter C	100 ppm	70 ppm	90 ppm	85 ppm	95 ppm	More accurate than meter A

There are many factors that affect precision and accuracy, including (but certainly not limited to) chemical and physical properties of the sample, weather (humidity and temperature are the two most influential factors), and the sensor technology.

Two other terms that need further explanation are bump test and calibration. A **bump test**, also known as a **field test**, involves exposing a monitor to a known gas, allowing the monitor to go into alarm, and then removing the gas. This verifies that the monitor responds to the gas.

Calibration, on the other hand, is used to determine whether a monitor responds accurately to a known quantity of gas. Calibration electronically corrects the sensor so that it reads the proper value.

All monitors have a **lag time** or, as it is better known, **reaction time**. Reaction time will vary depending on whether you are sampling with a pump. Monitors without a pump operating in a diffusion mode generally will have a 15 to 30 second lag time. Monitors with a pump have a typical reaction time of 3 to 5 seconds, but even this can vary from manufacturer to manufacturer.

Hand-aspirated pumps usually require 10 to 15 pumps to draw in an appropriate sample. When using sampling tubing, add 1 second of lag time for each foot of hose. Be sure to follow the manufacturer’s recommended lengths of hose to ensure that the pump operates correctly.

Just as the monitor has a reaction time, it also has a **recovery time**. Recovery time is the amount of time that it takes the monitor to clear itself of the air sample.

Relative response is a term used to describe the way the monitor reacts to a gas other than the one for which it was calibrated. Emergency responders commonly do not use this term. In order to maintain a high level of safety, each person operating an air monitor must understand relative response, as the monitor’s readings otherwise may be misleading.

All monitors are designed to be used for one specific gas, and it is usually the one for which it is calibrated. One might believe that we would need several hundred monitors to perform emergency response. Luckily, all monitors have a relative response curve. This relative response is the monitor’s reaction to other gases. The monitor’s manufacturer has tested the monitor against other gases and has provided a factor (relative response factor) that one can use to determine the amount of gases, other than the one for which the monitor is designed, that are present when sampling.

2.18.2 pH Determination

pH paper is one of the most useful tools that a responder can depend on. Because humans and electronic devices usually do not do well when exposed to corrosive materials, determining the pH of a released material is very important. We recommend that pH paper be one of the first basic items at a chemical release. The reasons are obvious: corrosive materials will burn you and may render any electronic instrument useless very quickly. The determination of the pH of hydrolysis material is one of the methods of detecting warfare agents. Most of the detection devices will work for a limited time in a corrosive atmosphere, but eventually will quit working, sometimes without the user’s knowledge. Fortunately for emergency response, pH is fairly easy to check. The most common method is the use of a multilane pH paper, which comes in various sizes and ranges. For emergency response, this multirange paper is more than sufficient, as it is not necessary for us to determine pH down to the 10ths; whole numbers are more than adequate for a quick assessment.

When dealing with an accident, it is important to sample for corrosives very early. When you know the status of the air, you can take steps to protect yourself and the other monitors.

pH paper comes in several different forms, but the most common is a 1/4-inch roll of paper, with a pH range of 1 to 12 or 0 to 13. Also available are individual strips that cover the range of 0 to 14, as well as individual numbers.

2.18.3 Oxygen Monitors

After pH testing, oxygen is the next most important sample; we need oxygen to survive, and the instruments need it to function correctly. Normal air contains 20.9 per cent oxygen; air containing less than 19.5 per cent is considered oxygen deficient and a health risk, and air containing more than 23.5 per cent is considered a fire risk. An oxygen sensor is an electrochemical sensor that has two electrodes within a gel-like material. When oxygen passes through the sensor it causes a chemical reaction, creating an electrical charge and causing readout to be provided on the monitor.

Oxygen monitor limitations

Most oxygen sensors will last only one year, since they are always working.

The optimal temperature for operation of an oxygen sensor is between 32° and 120°F (0° to 48.9°C). Between 0° and 32°F (-17.8° to 0°C) the sensor slows down; temperatures below 0°F can damage the sensor permanently. The operation depends on absolute atmospheric pressure, and calibration is required at the atmospheric pressure that you will be sampling. The manufacturer’s recommendation (and ours) is that you calibrate the sensor at the temperature, pressure, and weather conditions of the area that you will be sampling in.

Always consider that if an oxygen drop is noted on the monitor, one or possibly more than one contaminant is causing the reduced oxygen levels and another material (that is, toxic, flammable, corrosive, or inert) is causing the oxygen-deficient atmosphere. In oxygen-deficient atmospheres, any combustible gas readings will also be deficient and cannot be relied upon. In an oxygen-enriched atmosphere, the combustible gas readings will be increased and inaccurate.

2.18.4 Combustible Gas Indicators

Combustible gas indicators (CGI’s), also referred to as combustible gas sensors, have been used by the fire service and industry for many years. Most of the new CGIs are used to measure the lower explosive limit (LEL) of the calibration gas. CGIs are calibrated using a known gas and amount of concentration in air. When calibrated for methane, for example, the CGI sensor will read up to the LEL, and some of the new units will shut off the sensor when the atmosphere exceeds the LEL. There are CGIs that read above the LEL, many times combined with an LEL monitor that will read samples in per cent by volume. Landfills and some industrial applications need CGIs that read 100 per cent by volume because they often greatly exceed the LEL and need to monitor the higher levels.

The CGI reads up to 100 per cent of the LEL, so you must understand the readings it gives in terms of the specific LEL involved. If it is calibrated for methane, for example, and you are sampling methane, and the CGI reads 100 per cent, the actual concentration in that area is 5 per cent for methane (since the LEL for methane is 5 per cent). If your CGI gets a reading of 50 per cent, then the concentration for methane is 2.5 per cent.

Any flammable gas sample that passes over the sensor will cause a reaction how much of a reaction depends on the gas. Each CGI comes with a relative response curve for gases other than the one for which it is calibrated. The exact number of other gases referenced varies from manufacturer to manufacturer. To further complicate this issue, in situations involving a gas other than the specific one for which the CGI has been calibrated, some gases generate higher readings than their actual concentration and others lower readings. If the CGI reading is above the actual percentage, you are safe, but if it is below the actual percentage, then you may no longer be in a safe atmosphere, as you may have exceeded the LEL.

Table 18 **EPA atmospheric hazard action guidelines**

Atmosphere	Level	Action
Combustible gas	<10% LEL	Continue to monitor with caution
	10-25% LEL	Continue to monitor, but use extreme caution, especially as higher levels are found
Oxygen	<19.5%	Monitor with SCBA; CGI values are not valid
	19.5-25% (OSHA 23.5%)	Continue monitoring with caution; SCBA not needed based on O2 content only
	>25% (OSHA 23.5%)	Explosion hazard; withdraw immediately

The Environmental Protection Agency (EPA) has established action levels that provide a safe layer expressly because of the relative response curve problem. They have factored in the response curve problem and provided guidelines for us to follow.

The unfortunate thing about the action guidelines is that they were originally designed for hazardous waste sites (which are usually outside) and do not apply to a lot of what the fire service does. Is a building with >25 per cent of the LEL dangerous? Yes! But we are obligated to reduce the hazard (life hazard), so we may be forced under extreme circumstances to bend this guideline. So no matter what the gas is, even if you can't readily identify it, the worst case scenario at a reading of 25 per cent has you encountering a gas concentration that still would be below the LEL. You should remember the common response curves, or better yet, have them listed on the monitor, and look up the uncommon ones.

One of the nice things that manufacturers now are providing is automatic calculation of relative response curves. The MSA Passport Photo-ionisation Detector (PID), Toxi-Rae PID, and the AIM 3000 offer this feature. All three monitors have numerous response curves built in.

2.18.5 Combustible gas sensor types

The basic principle underlying most CGIs is that a stream of sampled air passes through the sensor housing causing a heat increase, conversely creating an electrical charge, and causing a reading on the instrument. There are four types of combustible gas sensors, and it is important when purchasing or using a monitor that you know its sensor type. Readings can and do vary among the four, and since your safety is in the hands of that instrument, you must understand how it works.

Whetstone bridge sensor

The most common sensor is a Whetstone bridge sensor, which is essentially a coiled platinum wire in a sealed sensor, which is heated. When the sample gas passes over the "bridge," it heats up that side of the bridge-heated platinum filament. Platinum is used because it can catalyse oxidation (combustion) reaction at relatively low temperatures and at low concentrations of flammable vapours. If the air sample contains any concentration of a flammable gas, the platinum filament will get hotter and increase its resistance to an electrical current in a nearly direct proportion to the concentration of any flammable content. The change in resistance is compared to a known constant resistance and the difference is converted to a meter reading. Newer and much better Whetstone bridge CGIs actually has two separate wire coils in the middle of the sensor. Both are heated with the sample gas passing over one of the "bridges." The sample gas, if flammable, will cause the bridge to heat up, causing a difference in the electrical resistance between the two bridges. This difference is reported on the readout of the CGI. Older Whetstone bridges may have problems in the following areas:

- Low-oxygen atmospheres - you must have good air to get a good reading. If there is less than 19.5 per cent O_2, your readings are going to be off. If the O_2 is high, the CGI reading will be high as well.
- Lead vapours (from leaded gasoline), sulphur compounds, silicone compounds, and acid gases can corrode the filament, which will cause altered readings.
- Exposing the CGI to high levels of gas may saturate the sensor and cause it to be useless for a long period of time.

The old Whetstone bridge CGIs (as well as many new ones) did not indicate when gas levels went above the LEL. In most cases, the CGI would indicate 100 per cent of the LEL for a very short time and then bounce back to 0 per cent, never to rise again: The bridge had burned out and would not function. Some monitors took 15 pumps of the air aspirator to get a reading (see discussion of response time), but nobody took the time to pump it 15 times and then move to a new location. When the monitor did hit 100 per cent of the LEL, it was based upon a sample taken somewhere in the building (Who knew where?), and if the operator caught the needle as it was jumping to 100 per cent and could therefore identify where the reading was obtained, he/she was lucky (most missed it). The new technology allows the sensor to read up to 100 per cent of the LEL, then shuts the sensor off, or if so equipped, will switch over to the CGI that measures percentage by volume methane. This is a marked improvement and will save many dollars in sensor replacement. The new CGI sensors should last a minimum of 4 to 5 years, although almost all manufacturers warrant them for only a year.

Catalytic bead

This sensor is essentially the same as the newer Whetstone bridge technology, but with some innovations. Instead of twists of wire forming a bridge, it uses bowl-shaped pieces of metal, typically coated with a catalytic material that aids in the efficient burning off of the gas sample. The sensor has two bowls, placed in the same fashion as the twists in the Whetstone bridge-one for sampling, the other for reading the change in the sampling bowl.

Metal oxide sensor

The metal oxide sensor, commonly referred to as an MOS, is new to the CGI market and is attracting a lot of attention. It is very sensitive, and its newness accounts for all of its perceived problems. If used correctly (and interpreted correctly), this sensor can provide clues/answers to many of our response questions. The MOS is a semiconductor in a sealed unit that has a Whetstone bridge surrounded by a coating of metal oxide. Heater coils provide a constant temperature. When the sample gas passes over the heated bridge, it combines with a pocket of oxygen created from the metal oxide. This reaction causes an electrical charge which causes the CGI to provide a reading. Some people have a problem with this sensor because it is very sensitive and will pick up almost anything that crosses it. Most MOS CGI's do not provide readout of the percentage, but only an audible warning or a number that is truly relative. If you spill a tablespoon of baby oil on the table and pass an MOS over it, you will get a reading. If you take an MOS into a room with 5 per cent methane, you will get a reading within a range for a flammable gas. Some monitors allow the MOS to read in percentages of the LEL, in addition to a general sensing range of 0 to 50,000 units.

The MOS reacts to tiny amounts, which is an outstanding feature, as most monitors are not this sensitive. It is generally not recommended that you purchase an MOS unit if you can afford only one combustible gas sensor. Instead, choose either Wheatstone bridge or catalytic bead. If a response team wants to enhance its capabilities further, then an MOS is a great addition to the air-monitoring capabilities.

Infra-red sensors

Infra-red sensors are new to the emergency response field and have some unique features which enhance the hazardous materials team's capabilities further. The infra-red sensor uses a hot wire to produce a broad range of wavelengths, a filter to obtain the desired wavelength, and a detection device on the other side of the sensor housing. The light that is emitted from the hot wire is split, one part moving through the filter, the other to the detection device to be used as a reference source. When a gas is sent into the sample chamber, gas molecules will absorb some of the infra-red light and it will not reach the detection device, which will read the amount of light reaching the detector. The amount of light reaching the detection device is compared and a reading is provided. The big advantage of an infra-red sensor is that it does not require oxygen to function. The device also is not affected by temperature, nor is it easily poisoned by high exposures. The disadvantages include cost and its many cross-sensitivities.

2.18.6 Toxic Gas Monitors

In this section we will limit our discussion to the toxic sensors used most commonly in three-/four-/five-gas units (LEL, O_2, toxic/toxic/toxic) to measure carbon monoxide (CO) and hydrogen sulphide (H_2S). Toxic sensors are available for a variety of gases: chlorine, sulphur dioxide, hydrogen chloride, hydrogen cyanide, nitrogen dioxide, and many others. By far the best-selling unit today is a four-gas unit that measures LEL, O_2, CO, and H_2S. This is a direct result of the confined-space regulation issued by the Occupational Safety and Health Administration (OSHA).

Most toxic sensors are electrochemical sensors which have electrodes (two or more) and a chemical mixture sealed in a sensor housing. The gases pass over the sensor, causing a chemical reaction within the sensor, and an electrical charge is created which causes readout to be displayed. All toxic sensors display in parts per million (*ppm*). Some toxic sensors use metal oxide technology and react in the same fashion as CGI metal oxide sensors.

The chemistry of hazardous materials can help clarify some of the problems related to toxic sensors. The periodic table plays an important role when dealing with toxic sensors. Its vertical columns contain families of elements, all of which share the same characteristics. We'll use the chlorine sensor as an example. Because chlorine belongs to the halogen family, which also contains fluorine (gas), bromine (liquid) iodine (solid), and astatine (solid), the sensor will react in a similar fashion to any of the halogens. If you don't know what you are sampling, you might misinterpret the results.

Table 19 **Gases interfering CO and H_2S measurements**

Acetylene	Sulphur dioxide	Nitrogen dioxide
Dimethyl sulphide	Propane	Methyl alcohol
Ethyl alcohol	Mercaptans	Isopropyl alcohol
Ethylene	Hydrogen sulphide	Hydrogen cyanide

Another problem is that other chemicals can cause interference with the sensor. One of the unusual things about interference is that for the CO sensor, one of the interfering gases is H_2S. Most CO/H_2S sensors are filtered/manufactured to eliminate the interference – some are not. At times a simple charcoal filter over the sensor makes all the difference in the world in obtaining accurate readings.

Photo-ionisation detectors

The photo-ionisation detector (PID) uses an ultraviolet (UV) lamp to ionise any contaminants in the air. Because the contaminant particles become ionised, they carry an electrical charge which can be read. In order to be read by a PID, the gas to be sampled must have the ability to be ionised, a characteristic called ionisation potential (IP). The unit of measurement of an IP is electron volts (*eV*). Various types of UV lamps are available; the most common are 10.2, 10.6, and 11.7 *eV*. In order to read a gas with a PID, the gas must have an IP less than the *eV* rating on the lamp. For example, in order to sample benzene, which has an IP of 9.2 *eV*, we must use a lamp of 9.2 or above. The 10.2 lamp would read benzene just fine. The PID cannot detect gases that have IP's above the lamp strength. Keep in mind that the PID is calibrated to a specific material (usually to benzene using isobutylene as the calibrating gas) so a relative response curve factor needs to be factored in here. PID's have the ability to pick up readings from things that are toxic, but also can detect baby oil, motor oil, gasoline, and many other hydrocarbons. Many liquid pesticides are 1 to 50 percent solution mixed with xylene, tri-methyl benzene, and emulsifiers, which are easily detected by the PID. Cleanup of most drum dumps results in finding drums of waste oil, fuel oil, and the like, so the PID is a valuable resource in protecting responders and the public from toxic risk materials.

The PID sometimes is referred to as a total vapour survey instrument. Because of its ability to detect a wide variety of gases in small amounts, it is becoming an essential tool of response teams. The PID will not indicate what materials are present (much the same as the CGI will not identify the specific material that is present), but when used as a general survey instrument, it can identify potential areas of concern and possible leaks/contamination. The instruments are used widely during underground storage tank (UST) removals. Because of their sensitive nature, they can detect small amounts of hydrocarbons in the soil. With "sick-building" calls on the increase, the PID is a valuable tool in identifying possible hot spots within the building. As all terrorism agents are thought to have ionisation potentials below 10.6 *eV*, the use of PID's will assist in the detection of terrorism agents. Currently, the military is testing the use of PID's against terrorism agents.

Table 20 **Percentage of volume to ppm conversion**

Percentage of volume	Equivalent ppm
1%	10,000 ppm
2%	20,000 ppm
5%	50,000 ppm
10%	100, 000 ppm
50%	500,000 ppm
100%	1,000,000 ppm

The biggest advantage of a PID is its sensitivity, as it reads from 0.1- to 2,000 *ppm*, with one brand reading from 0.1 - 10,000 *ppm*. Chemicals with a permissible explosive limit (PEL) or threshold limit valve (TLV) of less than 500 *ppm* are considered toxic, so the PID is useful in identifying these types of levels. The CGI monitor does not even begin reading until concentrations reach levels much higher than 500 *ppm*. The conversion from percentage of volume to *ppm* is provided in Table 20.

It is easy to see that one could be in significant trouble with regard to toxicity when a CGI sensor would not even provide an indication of a problem. The PID is used to look for small amounts of things in air, and CGI's are for the larger problems, most specifically the fire risk.

Flame ionisation detector

Although one manufacturer refers to its product as an organic vapour analyser (OVA), this instrument is a flame ionisation detector (FID) with the added benefit of a gas chromatograph. The FID works on the same principle of ionisation as the PID but has some additional capabilities. Instead of using UV light to ionise any gases that may be present, the FID uses a hydrogen flame to complete the ionisation process. The biggest advantage of the FID over the PID is its sensitivity - in some cases, it can read down to the parts per billion (ppb). Although its sensitivity is an advantage, it also can be an extreme disadvantage. Because it can read so many gases, you will generally get some type of reading that can be misinterpreted. Also, when a PID ionises a gas sample, it is a one-time chance for a successful ionisation. The FID, on the other hand, will ionise the sample continually, allowing for even greater results. Because the FID is using a flame to ionise the gas and the resulting release of carbon atoms is a repeatable event, the FID is a more accurate device than the PID. The FID also will read methane, which at high levels will alter the readings from a PID. The FID reads methane very well, actually down to 0.5 *ppm*. As with other instruments, this one needs good oxygen to work, and high wind conditions and some high concentrations may cause flame problems. The need to refill the hydrogen cylinder on the unit may prove cumbersome during long-duration sampling.

Gas chromatography/mass spectrometry

Gas chromatography/mass spectrometry is the next step for response teams to take after the use of an FID. Although it is not common today, increasing concerns about terrorism will make this practice more common in the future. Several companies produce field instruments that have some application in emergency response. The field instruments usually are coupled with a PID or an FID to assist with the sampling process.

The principle behind the gas chromatograph/mass spectrometer (GC/MS) is that it uses a column through which the sample is passed. Each type of gas in the sample has a varying degree of attraction to the material that makes up the column and a definite travel time within the column that is unique to that particular gas. When the material exits the column, the time that the travel took is compared to the library, and a match can be made, based on this property of unique travel times. With multiple gases present, each will "boil off" at differing temperatures causing an individual spike on a roll of paper (much like the heartbeats on a heart monitor). Each chemical has what is known as a retention time and will produce a spike at a specific time interval, which also helps identify the sample gas. The length and width of this spike can be used to determine the type of material when the printout is compared against known samples. The MS portions take the sample into a chamber and compare the mass of the gas sample against those in the library. It is the comparison that provides a definitive identification. The GC portion provides a close match, but the MS side of the machine provides the confirmation. The sampling time varies from sample to sample, but sampling sometimes can be completed in 10 to 20 minutes per sample.

GC/MS is one of the last resorts when dealing with unknowns, but to even begin to hazard a guess, the lab must have a comparison sample of the gas or liquid you want it to analyse for. A GC/MS cannot detect water, so if the sample contains water, the other components will be overstated unless the water content is independently measured and factored into the analysis calculations. Field GC/MSs are available, but are not readily used by response teams due to their highly technical nature. The response to terrorism will likely increase the need for field-ready GC/MS's, however.

Colorimetric sampling

Colorimetric sampling consists of taking a glass tube filled with a reagent (usually a powder or crystal) that is placed into a pumping mechanism which causes air to pass over the reagent. If the gas reacts with the reagent, a colour change should occur, indicating a response to the gas sample. Detection tubes are made for a wide variety of gases and generally follow the chemical family lines (that is, hydrocarbons, halogenated hydrocarbons, acid gases, amines, etc.). Although the tubes may be marked for a specific gas, they usually have cross-sensitivities (react to other materials), at times the most valuable aspect of colorimetric sampling.

Colorimetric tubes are used for the detection of known and unknown vapours. With sick-building calls becoming more and more frequent, the use of colorimetric tubes has greatly increased. It is unfortunate that this valuable tool in risk assessment is often forgotten or used incorrectly. Colorimetric sampling is not a simple task, and the user must be familiar with every aspect of the unit being used. The results one can obtain, however, are invaluable. Even if we cannot determine what material is present, colorimetric tubes can tell us which ones aren't present, which can be more important.

The chip measurement system (CMS) developed by Drager involves the use of bar-coded sampling chips in colorimetric sampling. A sampling chip is inserted into a pump. The pump recognises the chip in use and provides the correct amount of sample through the reagent. The pump, using optics and light transfer system reflective measurement, provides an accurate reading of the gas that may be present. While many of the chips are under development, there are about 10 available today for the common gases. The advantage to this system over regular colorimetric sampling is the fact that the reading is provided on an LCD screen in *ppm* and therefore needs no interpretation. The other colorimetric systems require a length and colour interpretation by a human, which at times is faulty. The disadvantage to the new system is that a general sensing tube is not available yet, nor can the system sample more than one gas at a time. Some systems have the ability to increase the sensitivity of a particular tube by reusing a tube after negative results, but the CMS does not allow this. The chips have 10 sampling capillaries which, after each is opened, cannot be reused, nor can the sampling range be enhanced.

Mercury detector

An instrument that is not in common use, but is occasionally required, is a mercury vapour detector, used to determine the level of mercury vapour in the air. One unit has a measuring range of 0.001 to 0.999 mg/m^3 of mercury. The unit has a gold film sensor that has an affinity to mercury. If the unit is placed in an environment that has mercury vapour in the air, the mercury will be attracted to the gold foil. As the mercury collects on the gold foil, the electrical resistance changes and causes a corresponding reading on the display. As the concern for the health effects of mercury releases continues to escalate, the use of these monitors also will increase. Some terrorism scenarios use mercury in an explosive device, and it is possible that mercury may be present at a terrorist accident.

Chemical classification kits

These kits are designed to identify and/or characterise solids, liquids, and some gases. These kits use colorimetric tubes to identify the gases. For solids and liquids, the kit uses a flowchart to sort through the various chemical families. Much like the colorimetric system, these kits rely on the fact that chemicals within the same family react in the same fashion. Using a series of tests, including mixing a sample with a large number of reagents, the user can, by the process of elimination, identify and/or characterise a sample.

The original instructions for the kits were cumbersome, but the instructions have improved dramatically over the years. The system does require specific training, and a background in chemistry helps. Frequent use or training is required to maintain proficiency. The EPA has developed a characterisation sequence that resembles a modified version of the commercial kit.

Some of the tests used in both kits will provide the framework for general risk categories. Typically, the one big area that is deficient in effective sampling is the identification of unknown solids. Some of the initial concerns with solids are:

- water reactivity
- air reactivity
- explosive characteristics (oxidisers)
- peroxidised materials
- toxicity (cyanide, sulphides)
- narrow identification to a chemical family or group

With liquids, some basic tests include:

- pH
- flammability
- toxicity
- water reactivity
- narrow identification to a chemical family or group

The use of detection devices and air monitors is by far the most important segment to the response to a potential industrial accident. By the use of detection equipment, responders can determine the presence of an HM, the amount of HM, and the spread of the HM. When confronted with thousands of patients, detection devices can determine if this group requires decontamination, or can be isolated for later treatment. Unfortunately this use of detection devices is not easy and, with the threat of potential accident, the pressure will be extreme. Good detection methods, using chemical and physical properties, are the formula for success.

2.19 Pathways of exposure

No chemical substance can cause adverse effects without first entering the body or coming to contact with it. There are four main ways (that is routes of exposure) for chemical substances to enter the human body:

- inhalation (breathing in)
- absorption (through the skin or eyes)
- ingestion (eating, swallowing)

Most chemicals used at the place of work may be dispersed into the air to form dust, mist, fumes, gas or vapour and can then be inhaled. In this way also workers who are not actually handling them but stay within their reach can be exposed to a mixture of chemicals from various sources.

Handling chemical substances without proper protection exposes the worker to the risk of absorbing harmful amounts of chemical through the skin. This usually happens when handling the chemical in liquid form. Dust may also be absorbed through the skin if it is wetted by, for instance, sweat. The capacity of different chemical substances to penetrate the skin varies considerably. Some substances pass through it without creating any feeling. Skin absorption is, after inhalation, the second most common route through which occupational exposure may take place.

The protective external layer of skin may be softened (by toluene, dilute washing soda solution, etc.) thus permitting other chemicals to readily enter the bloodstream (such as aniline, phenol, benzene, etc.).

Eyes may also absorb chemical substances, either from splashes or from vapours.

Dangerous chemicals can enter the body through ingestion as gases, dusts, vapours, fumes, liquids or solids. Inhaled dust may be swallowed, and food or cigarettes may be contaminated by dirty hands. Eating, drinking and smoking should be prohibited at a place of work where dangerous chemicals are used.

Whatever the route of entry, chemicals can reach the blood stream and be distributed all over the body. In this way damage can be caused at the site of entry as well as to organs distant from the exposed area.

Solid chemicals can be used in different forms: cakes, pellets, granules, powder wetted with oil, paste. Think about dust formation when choosing the form of a chemical.

Exposure assessment. The aim of the assessment is to obtain a realistic estimate of total human exposure, expressed in terms of dose per unit weight, for example, *mg/kg.*

In principle, the exposure of a human population could be assessed by representative monitoring data and/or by model calculations based on available information on substances with analogous uses and exposure patterns or properties.

Where existing substances are already used in processes with a high production volume, measured exposure data may be available. However, it is important to assess:

- the reliability of the measurements
- the representativeness of the measurements

The reliability of the data will be determined by the adequacy of the techniques used, the strategies and the quality standards used for sampling, analysis and protocol. While good quality data is preferred, that is, exposure data obtained by employing good occupational hygiene practice, in other cases it may be considered that data not up to this standard may be adequate.

With regard to the representativeness of the measurements, do they give a good picture of the exposures in the different locations? This requires consideration of the type of sampling, the location, the duration and the frequency.

However, in assessing exposure, representative and reliable data and the detailed information to use in modelling calculations may not be available in satisfactory detail.

As a general rule, in risk assessment the best and most reliable data should be given extra weighting. However, and particularly where data is of an unsatisfactory quality, it is often useful to conduct an assessment using "worst case" assumptions. If this indicates a risk that is of “no concern”, it can be stopped at that stage. However, if this is not the case, the assessment will have to be refined further.

Also, the degree of sophistication of an exposure assessment is likely to depend on the toxicity of the chemical. Thus a substance showing low toxicity may require only a qualitative, or at most a semi-quantitative, exposure estimation, whereas this is less likely to be the case where the compound is suspected to be of higher toxicity.

2.19.1 Types of exposure

We can divide the exposure of humans to chemical substances into three types:

- exposure in the workplace (occupational exposure)
- exposure from the use of consumer products (consumer exposure)
- indirect exposure through the environment

Indirect exposure through the environment can be particularly complex. Apart from direct exposures to air, soil and water, there can be indirect exposures through contamination of the food chain.

In some cases there will be contributions from all three types of exposure to the overall exposure value considered in the risk characterisation.

Exposure levels received by each of these groups must be made based on one or both of the following:

- available measured data (if possible)
- modelling

The predictions of the exposure levels should describe a reasonable worst case situation, covering normal use patterns and where consumers/workers may use several products containing the same substance; also upper estimates of extreme use and even reasonably foreseeable misuse. However, it should not cover exposures as a result of accidents or abuse.

In making the assessment, the best and most realistic data available should be given preference.

Where the outcome of the assessment is that the exposure is of “no concern”, particular care should be taken to be able to justify this assessment. This is particularly the case when dealing with the use of high volume materials in the workplace.

When carrying out an assessment, account should be taken of risk reduction/control measures that are in place.

Normally the exposure assessed will be an **external exposure,** that is, the amount ingested, in contact with the skin, inhaled, or the concentration in the atmosphere. Where the conclusion is that this level is “of concern”, it may be necessary to determine the **internal exposure,** that is, the amount taken into the tissues of the body, or its bio-availability.

2.19.2 Occupational exposure

The most common routes of exposure in the workplace are by inhalation or by absorption through intact skin. Dermal exposure may also result in local effects, such as irritation or dermatitis. The actual ingestion of substances is not normally a problem because of hygiene controls in the working environment.

Of primary importance in developing the assessment of occupational exposure is a full understanding of the processes and unit operations in which exposure occurs, and of the actual work activities resulting in exposure. With this background knowledge, the following questions have to be answered.

- What is the population of potentially exposed individuals?
- What are the magnitude, frequency and duration of inhalation and dermal exposures?
- What personal protective equipment and control methods are used to reduce or mitigate exposure?
- How effective are they at reducing exposure?

The overall assessment of each type of exposure should be repeated for all the various production processes and uses made of the chosen chemical. From knowledge of the frequency and duration of exposure the “worst case” should be highlighted.

If “real” data are missing for a chosen substance, as an alternative to modelling it may be possible to substitute data from another chemical with a similar pattern of exposure.

Major factors affecting exposure potential include:

- size of the activity
- physical characteristics of the activity
- time of exposure

Size of the activity. The greater the quantity of a substance involved or the higher the concentration in solution, the greater the potential for exposure is likely to be. Any potential hazard from 10 tonnes is likely to be considerably greater than that from 10 mg.

Physical characteristics of the activity. Particle size of a solid and the volatility of a liquid are also likely to affect exposure, as is the presence of barriers to the exposure and containment of the substance away from human contact. Procedures involving elevated temperature, particularly with substances with significant vapour pressures, may engender an enhanced inhalation exposure.

Time of exposure. The duration and frequency of exposure to an activity will also be a factor – the longer the time of exposure the higher the exposure potential.

The two main sources of occupational exposure are inhalation and dermal exposure, and these are affected by the above characteristics as described below.

Inhalation exposure. Gases, fumes and vapours can be absorbed in the respiratory tract. The extent of absorption will depend on the atmospheric concentration of the substance and on its ability to cross cell barriers.

The behaviour of solid particulate will depend on their particle size. Dust and fibres of particle size < 0.1 μm behave in the same way as vapours; where the particle size is > 10 μm they become trapped in the upper respiratory tract and may be swallowed. Particles of intermediate size < 10 μm (known as PM10 dusts) may penetrate deep into the lungs and reach the alveoli. There they may stay for periods as long as several years, since alveolar membranes have no cilia to move the particles out of the lungs towards the pharynx. However, it should be noted that when wet (with the exception of “smogs”), inhalational exposure is negligible – in contrast to the potential exposure from a dry dust.

Because of the importance of inhalation exposure in the workplace, in a number of countries limit values in the workplace have been established. These are often based on those issued by the American Conference of Governmental Industrial Hygienists (ACGIH) and are usually defined in terms of a maximum permissible eight-hour time-weighted average (TWA) concentration of a substance in gaseous, vaporous or suspended form in the workplace. The term exposure refers to the presence of the substance in the air within the breathing zone of a worker. This figure is an upper limit, and in normal practice actual exposures should be kept as low as possible. For certain particularly toxic compounds, the limit is given as a maximum permissible concentration that should never be exceeded. This latter concentration is referred to as a “ceiling” value or concentration in some countries.

An increase in surface area of a liquid or solid can also increase exposure. Such processes are the mixing, agitation and pouring of liquids, or the mixing together of dry and dusty solids.

If the process is completely enclosed the exposure to workers can become negligible, and conversely if there is no enclosure the exposure will be increased. Very often there is partial enclosure of the process, and an intermediate exposure will result.

Dermal exposure. With liquids which are dermal hazards, the less volatile the liquid the greater its exposure potential. Under normal conditions a highly volatile liquid is likely to have evaporated from the skin before significant amounts have been absorbed through the skin. The exposure will also be greatly reduced if the activity is completely contained or is separated from the skin by a protective barrier, such as that of protective clothing.

With solids, the more finely divided it is, the greater it’s potential to contaminate the skin and increase the exposure. Again, this exposure can be greatly reduced by appropriate barriers.

Under conditions of occupational exposure, the evidence suggests that the amount of a chemical absorbed through the skin can often make a substantial contribution to the daily dose. The large surface area of the skin and its direct contact with the environment will encourage this. Such exposure can arise either from normal everyday contact, or following accidental spillage.

As an absorption route it appears to be of particular significance in agricultural workers involved in pesticide application. Drenched clothes, inadequate protective equipment and unsafe spraying methods have resulted in a number of cases of intoxication mainly due to skin absorption, particularly in hot environments where protective clothing, if available, might tend to be discarded. It should be remembered that any contamination of the inside of protective clothing might be particularly dangerous.

2.19.3 Measurement of exposure

External exposure. In most situations it is unlikely that continuous monitoring of a potential hazard can be carried out. It is therefore necessary to resort to sampling measurements, by their nature intermittent, to obtain a picture of the exposure in different areas. Decisions have to be made about what is going to be measured, where it is going to be measured and for how long and how often.

Sampling regimens can be of two types:

- to aid the engineering control of in-plant emissions
- to assess the likelihood of risk to workers’ health

Sampling for the first purpose is concentrated on the sources of contaminant emissions, and for the second in the area where people work. The duration of each test sample should be long enough to smooth out short-term fluctuations.

Workplace air monitoring. This technique can give valuable information about the degree to which workers are exposed to an external airborne hazard. It consists of the periodic or continuous analysis of the workplace atmosphere, and can also be used to measure the values to which the worker is exposed in his personal breathing zone as he moves around by the use of a sampling device attached to his person.

This device can be in the form of a filter or, particularly where chemical vapours are present, of an indicator tube that changes colour when the vapour interacts with its contents, giving a semi-quantitative measure of exposure. More sophisticated devices can of course be used.

The level of contaminant found on the filter or the reading from the indicator tube can be compared with any limit values and appropriate action taken should the readings indicate an excessive exposure.

Skin exposure. In most cases estimates of skin exposure to chemicals have to be obtained from modelling, although more direct methods, none completely satisfactory, have been used.

One technique is the use of wipe samples from a known area of the skin surface, followed by their analysis for the substance of interest. However, uncertainties arise both from how quickly the substance is absorbed and also the extent of its recovery from the skin by this technique.

Methods of this type have been particularly useful for chemicals that are only slowly absorbed through the skin, such as polychlorinated biphenyls, polyaromatic hydrocarbons and certain pesticides.

The World Health Organisation (WHO) has developed a standard protocol for pesticide exposure involving disposable overalls and gauntlets, and pads attached to clothing and skin that can be analysed for the pesticide after spraying. An alternative technique is to use a fluorescent tracer added to the pesticide to detect and analyse the extent of clothing and skin contamination.

Dermal exposure is normally assessed as a potential dose rate predominantly to the hands and forearms. These have an area of approximately 2,000 cm^2. Typical units of exposure are mg/cm^2 of skin per day.

Biomarker

A biomarker is formally defined as a "parameter that can be used to identify a toxic effect in an individual organism and can be used in extrapolation between species, or as an indicator signalling an event or condition in a biological system or sample and giving a measure of exposure, effect or susceptibility".

Internal exposure – Biomarkers. To determine the internal exposure of a human to a chemical substance, analysis of tissues and body fluids can be carried out. These are aimed at measuring levels of the substance itself, of its metabolites, or of enzymes and other biological substances or responses affected by the substance. The determination of such substances – known as **biomarkers –** provides an index of the internal dose of the substance and hence of internal exposure.

The term can be used in a very broad sense to include a whole range of biological effects reflecting an interaction between a hazard and human biology, for example, it may be functional and physiological, it may be biochemical at the molecular level, or it may be a molecular interaction.

It is important that before they are used in a Risk Assessment, the relationship between the biomarker, the exposure and the health outcome must be established, and this may prove a complicated process.

Although often less convenient than methods of external exposure assessment, they do provide direct evidence for the exposure of individuals in a population to a particular substance, for example, an organic solvent in exhaled breath, lead in bone, or fatty tissue storage of chlorinated hydrocarbons. Quantitative measurements may permit the determination of a dose-effect relationship, particularly if the toxicokinetics of the substance are well established.

The measurement may be used for screening and, if repeated at timed intervals, for monitoring either an individual or a group.

In occupational risk assessment, biomarkers provide a **supplementary** means of reviewing the effectiveness of the control measures in use.

Biomarkers of exposure or effect may be used to evaluate compliance with advice for minimising exposures or to indicate the need for remedial measures, for example, the reduction of lead exposure in a public health context.

Consumer exposure. A consumer product is one that can be purchased from a retail outlet by members of the general public, and it may comprise the substance itself, some mixture containing the substance, or an article containing it. Consequently, any person purchasing the product may be exposed to any hazard associated with the substance, and a complicating factor is that the purchaser could be of any age or state of health, or of either sex.

In some cases a substance might be used in the production of a preparation or material, but not be present in the final product. Further assessment of consumer exposure to that substance through that product would then obviously not be necessary.

We have seen previously that an occupational exposure to a particular substance under normal conditions would involve only inhalation and dermal exposures. With exposure to substances in consumer products, the ingestion route may be relevant.

Also, in contrast to occupational exposure, the pattern of use of a consumer product is likely to be much more variable. The two relevant factors are the frequency of use and the quantity used on each occasion.

In assessing the exposure, much of the discussion of occupational exposure will be relevant. Again, “real” data are preferred, but it is likely that “estimation” methods will have an even greater part to play – reference has already been made to the computerised models for the assessment of consumer exposure to household products produced by the US EPA.

Indirect exposure via the environment. The third potential source of exposure of humans to chemical substances is indirectly via the environment – by ingestion of food and water, and by inhalation of air. In abnormal circumstances where there is pollution of the soil by the substance, dermal contact with the soil and its ingestion might also have to be considered as sources of exposure.

In determining this indirect exposure, the following stepwise procedure is followed:

- assessment of concentrations in intake media (food, water, air and soil)
- assessment of the intake rate of each medium
- determination of the intake from the concentrations and intakes in the media (if necessary using a factor for the bio-availability through the route of intake)

2.20 Health and medical consequences

2.20.1 What are the responses of a system when exposed to poisons?

The human body needs, in very small quantities, some of the chemicals that are poisonous in large doses. This applies, for example, to some metals, such as copper, magnesium and manganese, which pose a problem in the places of work. The adverse effect is strongly related to the dose. The ultimate effect is death. Usually the effects of toxic chemicals are less severe, from altered food consumption to serious health problems.

The harmful effects of chemical substances depend on the toxicity and the exposure to that chemical. Toxicity is a property of the chemical substance, while the exposure depends on the way the chemical is used. The level of exposure depends on the concentration of the hazardous chemical and on the period of contact time. Many substances do not give any warning by odour, even though they may be present at dangerous concentrations in the workplace air.

2.20.2 Acute effects – chronic effects

The effects may be acute: after a short exposure an immediate effect may be experienced. Chronic effects usually require repeated exposure and involve a delay which is observed between the first exposure and appearance of adverse health effects.

A substance may have acute and chronic effects. Both acute and chronic conditions can result in permanent injury.

Injury from exposure to a chemical substance can be temporary, that is, reversible. It will disappear when exposure to that chemical stops.

Exposure to solvents may cause contact dermatitis, headache or nausea. These effects could be both acute and temporary. Solvents can also cause chronic effects and result in an irreversible, permanent injury to the nervous system.

2.20.3 Local effects – systemic effects

Hazardous substances may cause local effects. Acute local effects may include corrosive injuries from acids and bases or lung injuries from inhaled gases such as ozone, phosgene and nitrogen oxides.

Many other gases cause adverse effects only after they have been inhaled repeatedly over a long period of time. Low concentrations of a gas may also be effective in this way. A persistent irritation of the respiratory system can arise from exposure to gases such as sulphur oxides, hydrogen fluoride and hydrogen chloride.

Once the hazardous substance has entered the blood circulation, it may be distributed to all parts of the body. It will reach the liver, which is the most important detoxification organ of the body. The liver attempts to convert the toxic agents to less toxic ones or to the ones useful to the body. This process is called metabolism. Some substances such as alcohol and carbon tetrachloride can damage the liver. The body excretes unwanted chemicals. The kidneys filter them out of the blood circulation, which is the main way that the body excretes poisons, but in doing this, they can be damaged by toxic substances such as carbon tetrachloride, ethylene glycol and carbon disulphide. Cadmium causes permanent damage to kidneys.

Other means of excretion are via faeces, sweat and through lung exhalation.

The nervous system is sensitive to chemicals. The adverse effects may be on the central nervous system or on the nerves that transport impulses to other parts of the body. Organic solvents are commonly used at work and are known to be able to affect the nervous system. Many other substances may behave in the same way such as carbon disulphide, mercury, lead, manganese and arsenic.

Our body has a considerable capacity to excrete, to render dangerous substances harmless, and to protect us. However, our defence system can be overloaded by repeated heavy exposure so that it no longer fulfils its function. The body stores the harmful substance which may consequently result in health problems.

Lead is an example of a substance for which removal from the body takes a long time. Cadmium is an example of a substance that is not processed by the body at all, and once it has entered it will stay there.

2.20.4 Human body

The effects may be immediate or delayed, and they may be reversible or irreversible toxic effects.

Local/systemic toxicity

There are two main ways in which chemicals may exert their effects. Local effects occur in the area of the body which has been in contact with the chemical. Examples are injuries from acids or lung injuries from inhaled reactive gases. Systemic effects occur after the chemical has been absorbed and distributed from the entry point to other parts of the body. Most substances produce systemic effects, but some substances may cause both types of effects. An example is tetraethyl lead, which is a gasoline additive and produces skin effects at the contact site. It is absorbed and transported into the body causing typical effects on the central nervous system and on other organs.

Target organs

The degree of the toxic effect is not the same in all organs. Usually there are one or two organs which show the major toxic effect. These are referred as target organs of toxicity of the particular substance. The central nervous system is the target organ of toxicity most frequently involved in systemic effects. The blood circulation system, liver, kidneys, lungs and skin follow in frequency of systemic effects. Muscle and bones are the target organs for a few substances. The male and female reproduction systems are vulnerable to many substances.

Skin is the largest organ in the human body, 1.5 - 2 m^2 in area. It provides a protective cover to the body but can fail if the load is overwhelming. A number of substances can penetrate healthy intact skin and enter the blood circulation. Phenol is a substance that may even result in death after exposure and penetration through the skin. The vast majority of work-related skin diseases are contact eczemas, irritation and inflammation of the skin. This condition can be either a non-allergic or allergic reaction to exposure to chemical substances. Examples of common contact sensitisers are several colorants and dyes, metals such as nickel and its salts, chromium and cobalt salts and organomercuric compounds, monomers of a number of acrylates and methacrylates, rubber additives and pesticides. In practice chemical skin injury is also influenced by environmental conditions such as humidity and heat. The lung is the major route through which toxic substances in the workplace enter the body. It is also the first organ to be affected by dusts, metal fumes, solvent vapours and corrosive gases. Allergic reactions may be caused by substances such as cotton dust, TDI (toluene diisocyanate, used in the manufacture of polyurethane plastics), and MIC (methylisocyanate, used in production of carbaryl insecticide). In a catastrophic chemical accident in Bhopal, India, in 1984, more than 2000 people died from exposure to MIC. Allergic reactions may result from exposure to bacteria or fungi: this is the case in allergies from handling stocked hay (`farmer’s lung’) or dried sugar cane. Dust in the lung causes a condition called pneumoconiosis. Pneumoconiosis is mainly a problem for workers exposed to the dust of silica (quartz) and asbestos, and is the commonest non-malignant occupational lung disease throughout the world. Other substances, such as formaldehyde, sulphur dioxide, nitrogen oxides and acid mists may cause irritation and reduce breathing capacity.

The nervous system, the `mystery of matter and mind’, is sensitive to the hazardous effects of organic solvents. Some metals affect the nervous system, especially heavy metals such as lead, mercury and manganese. Organophosphate insecticides such as malathion and parathion interfere severely with information transmission (chemical neurotransmitter function) in the nervous system, leading to weakness, paralysis and sometimes death.

The blood circulation is a target for the adverse effects of solvents. Blood cells are mainly produced in the bone marrow. Benzene affects the bone marrow; the first sign is mutation in the blood cells called lymphocytes. To study mutation, lymphocytes are cultured in the laboratory to observe specific types of cellular changes. Lead, in the form of the metal or its compounds, is another classic example of a chemical that may cause blood problems. Lead in the blood may inhibit certain enzyme activities involved in the production of haemoglobin in red blood cells. Chronic lead poisoning may result in a reduced ability of the blood to distribute oxygen through the body, a condition known as anaemia. The liver is the largest of the internal organs in the body and has several important functions. It is a purification plant which breaks down unwanted substances in the blood.

The liver has a considerable reserve capacity; symptoms of liver disorder appear only in serious diseases. Solvents such as carbon tetrachloride, chloroform and vinyl chloride, as well as alcohol, are hazardous to the liver. The kidneys are part of the body’s urinary system. They have the task of excreting the waste products that the blood has transported from various organs of the body, of keeping the fluids in balance and of ensuring that they contain an adequate blend of various necessary salts. They also maintain the acidity of the blood at a constant level. Solvents may irritate and impair kidney function. The most hazardous to the kidneys is carbon tetrachloride. Turpentine in large quantities is also harmful to the kidneys: `painter’s kidney’ is a known condition related to occupational exposure. Other well-known kidney-damaging substances are lead and cadmium.

2.20.5 LD50 and LC50

For different substances the dose needed to produce an adverse effect varies widely. LD50 values are used to compare acute toxicity.

Classification may be based on the LD50 and LC50 values. The assessment of the effects is tested in laboratories using animals, mainly rats, mice and rabbits (Table 21).

The test substance or preparation may be applied to the animal orally, under the skin, by inhalation, into the abdomen or into the vein. LD50 and LC50 are the parameters used to quantify the results of different tests so that they may be compared.

- LD50 is the abbreviation used for the dose which kills 50% of the test population
- LC50 is the abbreviation used for the exposure concentration of a toxic substance lethal to half of the test animals
- LD50 is expressed in milligrams per kilogram of body weight of the test animal (which must be mentioned)
- LC50 is expressed in millilitres per kilogram of body weight of the test animal (which must be mentioned), exposed to the substance by inhalation during a specified period. The variation in the numerical values of LD50 and LC50 is wide.

It is important to mention the species on which the test was conducted because the numerical values of LD50 and LC50 depend on several factors, such as the biological system or animal, strain, sex, age and diet. The LD50 of DDT insecticide administered orally is 87 *mg/kg* of body weight for a rat but 150 *mg/kg* of body weight for a dog. The LD50 for dioxin is 0.02 *mg/kg* of body weight for a rat and 0.001 *mg/kg* of body weight for a dog, that is, the rat is twenty times more tolerant than the dog.

The assessment of how a human system would react is not a straightforward estimation from the animal tests. However, the animal test gives an idea of the level of the toxic effects.

Table 21 **Ingestion's studies on the rat - Variation in LD50 values**

Substance	LD50 (mg/kg, oral, rat)
Vitamin C	11 900
Ethyl alcohol (`alcohol')	7 060
Citric acid	5 040
Sodium chloride (table salt)	3 000
Ferrous sulphate	320
Dieldrin	38
Parathion	2
Dioxin (contaminant in herbicide)	0.02

Limit values

In order to control toxic effects, there is a need to set priorities, goals and strategies. In places of work one way is to set limit values to guide the users. Occupational limit values are based on the best available information from industrial experience, from experimental laboratory studies and from accidents. They are informed and negotiated compromises, not fixed safety standards.

There are different kinds of limit values. The TLVs (threshold limit values) are published by the American Conference of Governmental Industrial Hygienists (ACGIH) and concern the airborne concentrations of hazardous substances. They set a limit concentration below which it is believed that nearly all workers can be repeatedly exposed day after day without adverse effect. The TLVs are regularly reviewed and corrected when new information becomes available.

TLV-TWA (threshold limit value - time weighted average) is a time-weighted average concentration for an eight – hour working day or 40 hours a week to which nearly all workers may be repeatedly exposed without adverse effect.

TLV-STEL (threshold limit value – short term exposure limit) is the concentration to which workers may be exposed for a short time (usually 15 minutes) without suffering from irritation, long-term or irreversible tissue damage or impairment likely to increase accidental injury, affect self-rescue or reduce work efficiency. Daily TLV-TWA values should not be exceeded.

TLV-C (threshold limit value – ceiling) is a concentration that should not be exceeded at all during work exposure.

Allergic reactions

An allergic reaction, or sensitisation as it is also called, may appear after repeated contact to a substance. Once the sensitisation has bee produced, even very low doses can provoke a reaction. The different allergies are numerous, varying from minor skin irritation to very severe or even fatal reactions.

The pattern of sensitisation varies according to the species. In humans, the skin and the eyes are the most common areas of allergic response, whereas, for example, in guinea pigs reactions are more common in the respiratory system.

Interactions

The effect of simultaneous exposure to two or more substances may differ from a simple additive effect (1+1=2). Organophosphate pesticides, such as dialiphos, naled and parathion, are examples of chemicals where the combined effect is the sum of the effects observed when the chemicals act individually.

The effect can be more than the sum of the individual effects of two chemicals (for example, 1+1=4). An example of an increase in risk is with asbestos fibres and cigarette smoking. They act together: the risk of developing lung cancer after exposure to asbestos fibres is forty times greater for a smoker than for a non-smoker. Another pair of the chemicals where the combined risk is greater than a mere additive effect is solvents, trichloroethylene and styrene.

The adverse effects of two substances may counteract one another (1+1=0). This effect is used to find an antidote to a poison.

In other cases, a substance may not cause harm on its own but may make the effect of another chemical much worse (0+1=3). For example, two commonly used solvents, isopropanol and carbon tetrachloride have this kind of joint effect. Isopropanol, at concentrations which are not harmful to the liver, increases the liver damage caused by carbon tetrachloride.

In some cases, when the exposure to a substance is repeated, the body may decrease its sensitivity to the substance, that is, it increases its tolerance to it.

The environment

The environment has a certain capacity to biodegrade toxic substances. However, some substances are resistant to decomposing processes. The adverse effects increase with the concentration of these substances and their accumulation in food chains.

In the natural environment, large numbers of potentially toxic substances are present. In some cases, when the substance is on its own it would cause no harm but it may interact with other toxic substances or, under specific conditions, it may be concentrated or transformed to a more dangerous compound.

An example of an air pollution reaction is the production of photochemical smog. Chlorinated hydrocarbons such as DDT and dieldrin have similar chemical and biological effects. When present together they lead to more serious effects than when acting separately.

To assess the effects of toxic substances in the environment some indicators of ecotoxicity are used.

In laboratory, fish and insects called Daphnia (water-flea) are used to test acute toxic effects in the aquatic environment. Green algal species are also used in the assessment of water pollution.

3. Nuclear and Radiological Accidents

The nuclear accident at the Chernobyl reactor in 1986 shocked the world. More than 100,000 people were evacuated from the contaminated area, about 5 million have been exposed. In France, Germany, Poland and other European countries radiation protection measures have been implemented. For this reason nuclear and radiological hazards are discussed in separate chapters.

In all human activities the saving of life or prevention of serious injury have the highest priority. Remember – you cannot see radiation even at a very high dose, which could cause deterministic effects.

International experts have developed the principles of radiation protection and safety on which the International Basic Safety Protection against Ionising Radiation Standards are based. The main principles are as follows:

- practices that entail or could entail radiation exposure should only be adopted if they yield sufficient benefit to the exposed individuals or to society to outweigh the radiation detriment they may cause or could cause (that is, the practices might be justified)
- individual doses due to the combination of exposures from all relevant practices should not exceed specified dose limits
- radiation sources and installations should be provided with the best available protection and safety measures under the prevailing circumstances, so that the magnitudes and likelihood of exposures and the numbers of individuals exposed will be as low as reasonably achievable, economic and social factors being taken into account, and the doses they deliver and the risk they entail will be constrained (that is, protection and safety should be optimised)
- radiation exposure due to sources of radiation that are not part of a practice should be reduced by intervention when this is justified, and the intervention measures should be optimised; the person legally authorized to engage in a practice involving a source of radiation should bear the primary responsibility for protection and safety

3.1 Radioactivity

Radioactivity is a phenomenon of radioactive decay of the nucleus.

Radioactive decay is the ability of a nucleus to be spontaneously transformed into another nucleus or into the same nucleus with less energy. The extra energy is released by emitting particles (alpha, beta, gamma, neutron or other).

3.1.1 Main properties of atoms and nucleus

Atom structure

All materials are composed of atoms. An atom consists of a positive charged nucleus and negatively charged electrons, enclosing it. The atom has no electronic charge. In 1911 Ernest Rutherford showed that mass of the atoms was mainly concentrated (99.9%) in the nucleus.

The size of an atom approximately equals to 10^{-10} m.

The charge of one electron equals to 1.6×10^{-19} *Coulomb (C)* or in relative units to –1.

Structure of nuclei

The size of the nucleus is in the order of $10^{-15} \div 10^{-14}$ m. The charge of the nucleus Z is positive and equal to the serial number of the current chemical element in the periodic table of elements or number of its atomic electrons. For example, charge of the nucleus of the oxygen atom is equal to +8 relative units.

The nucleus consists of nucleons: protons and neutrons.

Proton: is the nucleus of hydrogen, a stable particle.

The proton is a stable particle and does not change its own characteristics in time. The charge of one proton is equal to +1. The mass of one proton is equal to $1.673\text{x}10^{-27}$ kg or 1.00782 u (atomic mass unit). 1 u amounts to 1/12 of mass ${}^{12}C$ atom and equals to $1.661\text{x}10^{-27}$ kg. The number of protons in a nucleus is equal to the number of electrons in an atom.

Neutron: is a neutral particle. The Neutron is an unstable particle outside of the nucleus, it decays into a proton, electron and antineutrino. Its average lifetime is approximately 15 minutes.

Inside a stable nucleus, the neutron is a stable particle. Its charge is equal to 0 (uncharged). The mass of one neutron is approximately equal to the mass of one proton: $1.675\text{x}10^{-27}$ kg or 1.00786 u.

The proton and neutron are characterized by "*spin*" – internal moment.

The charge of the nucleus is equal to the number of protons in nucleus. The number of protons and neutrons in the nucleus is called the atomic mass number *"A"*.

Definition of isotopes

Different atoms, the nuclei of which contain the same number of protons, are named "*isotopes*".

Because the number of protons determine the number of electrons and therefore element's' chemical properties, isotopes have identical chemical properties. It should be mentioned that physical properties of isotopes could be essentially different. Some of them are stable; others can decay and emit particles (they are radioactive).

For example, in the real world there are four well-known carbon isotopes with A = 11, 12, 13, 14. Carbon isotopes with atomic mass numbers 12 and 13 are stable. Carbon isotopes with atomic mass number 11 and 14 are radioactive.

Therefore, if we are interested in atoms not only from the point of view of their chemical characteristics, then we talking about it as a nuclide. We start use term nuclide or radionuclide and will add atomic mass number. For example: carbon-14, cesium-137. Nuclide can be determined also by symbol with specification of it charge and number of neutrons.

For example: ${}^{14}_{6}\mathrm{C}_{8}$ ${}^{137}_{55}\mathrm{Cs}_{82}$

The upper left index is the atomic mass number, the left sub-index is the charge of the nucleus (number of protons) and the right sub-index is the number of neutrons.

The radius of the atom nucleus depends on the atomic mass number **A** and is equal to:

$$r = r_0\sqrt[3]{A}, \qquad \text{where } r_0 = 1.35\times10^{-15}\,m \tag{1}$$

As nucleons, nuclei have spin, which can be determined by their own nucleon spins and by their movement in the nucleus. If the nucleus has an even number of protons and an even number of neutrons, then the spin of that nucleus is equal to zero. Otherwise, the spins and movement of the odd nucleons determine it.

Energy characteristics

The nucleons in the nucleus are in constant movement. The nucleons in the nucleus have different velocity of movement and different energies. The sum of nucleon energies determines the full energy of the nucleus (but not equal). According to quantum laws the full energy of the nucleus is a discrete value; the nucleus can have only certain energy values.

A nucleus with minimal possible energy is in a *"ground state"*, otherwise it is in an *"excited state"*.

Excitation energy: is energy equal to subtraction of current energy of the nucleus and energy of the nucleus in the ground state.

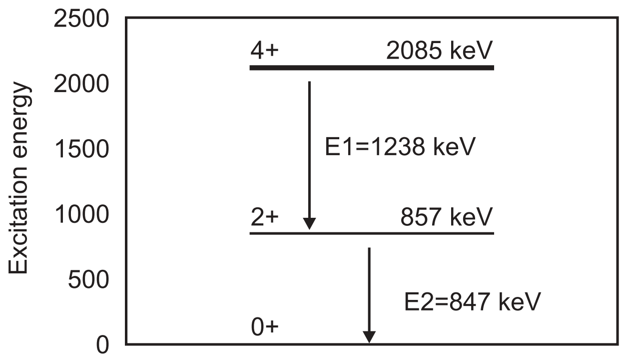


Fig. 3 **Excite states of Fe-56**

γ-quantum or **γ-ray** is the electromagnetic wave having a very short wavelength in comparison to other electromagnetic waves such as visible light, heat ray, and radio wave, which can be escaped from the nucleus during radioactive decay.

A set of the excitation states for the given nucleus can be represented as a graph (Fig. 3). Zero excitation energy on that graph represents the nucleus in a ground state. The electron Volt (*eV*) is the main energy unit in nuclear physics ($1eV=1.6x10^{-19}$ *Joule* *(J)*, 1 *MeV*=10^6 *eV*, 1*keV*=10^3 *eV*). The excite state of the *Fe-56* atomic nucleus is presented in Fig. 3.

Because of certain laws, which are not the subject of that chapter, γ-rays of certain energies will escape from an exited nucleus until the nucleus reaches a ground state. For example, if the *Fe-56* atom nucleus is in an excited state with excitation energy equal to 2,085 *keV*, from that nucleus can escape γ-ray with energy equal to 1,238 *keV* and after that γ-ray with energy equal to 847 *keV* or one γ-ray with energy equal to 2,085 *keV*.

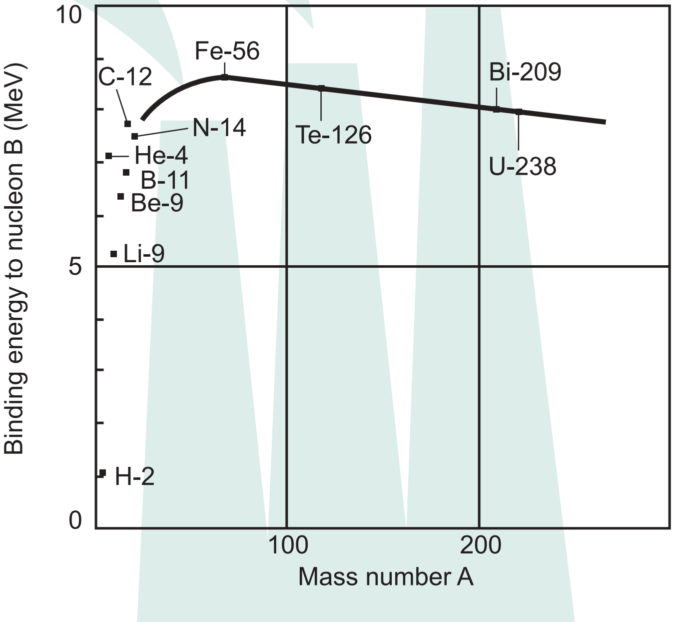


Fig. 4 **Dependence between the binding energy per nucleon B *(MeV)* and the atomic mass number A**

Emission of γ-rays from the nucleus is not a unique process of change of the nucleus state. Excitation energy can be transferred to a nearby atomic electron.

Binding energy per nucleon is another fundamental value for nuclear physics.

Binding energy of the nucleus is energy, which should be expended to liberate all nucleons from the nucleus.

Binding energy per nucleon *(B)* is equal to the binding energy of the nucleus divided by the number of nucleons in the nucleus (atomic mass number *A* of nucleus).

Binding energy per nucleon ranges from 1 *MeV* for *H-2* to 8.7 *MeV* for *Fe-56*. Binding energy per nucleon *B* is a measure of nucleus stability. If two nuclei with an equal number of nucleons have a different value *B*, then the nucleus with less *B* favours a change of its current state to become a nucleus with a higher value of *B*. More energy should be spent to liberate all nucleons from nucleus as less energy of nucleus. During the process of energy dissemination the γ-ray will escape from the nucleus.

If nucleus of *U-238* with *B*=7.5 *MeV* is to be divided into parts, then *B* of the one part (new nucleous) will be 8.5 *MeV* (Fig. 4). In such process about 1 *MeV* will be produced for each nucleon. For 200 nucleons it will be about 200 *MeV*. This fact is the basis for nuclear energy production technologies.

3.1.2 Laws of radioactive nuclei transformation

In 1905 Einstein discovered the mass-energy equation ($E = m \times C^2$). In that equation *E* is energy, *m* is mass, and *C* is the velocity of light. This is the main law of mass and energy equivalence.

As it was mentioned, if one can try to separate all nucleons in nucleus, than one should spend some energy for this purpose. Therefore the nucleus mass *M (A, Z)* should be less than the sum of masses of all nucleons in the nucleus.

The most common types of radiation are attributed to radioactive decay are alpha, beta and gamma rays.

Gamma rays

Gamma (γ) rays originate from atomic nuclei. Electromagnetic waves have no mass; essentially, an individual wave or photon consists of oscillating electric and magnetic fields, which are propagated together through space. All photons travel at the velocity of light. Their energies, however, vary over a wide range.

The gamma decay appear because the nucleus can change its excited state to an excite state with less energy or to a ground state. The energy of the gamma ray is equal to the subtraction of energy of the resulting state from the energy of the initial state of the nucleus.

The intensity of gamma rays is determined by quantum characteristics of the initial and resulting state of the nucleus and by its spins.

The energies of photons are normally expressed in terms of electron volts, usually millions of electron volts *(MeV)*.

The energy of gamma photons is very important because this is their only property, which varies in such a way as to affect their behaviour. The energy of a photon has tremendous influence on its ability to penetrate matter.

Many types of nuclear transformations are accompanied by the emission of gamma rays. For example, alpha and beta decay of many radionuclides is frequently accompanied by gamma rays. When parent radionuclide decays to a daughter radionuclide, the nucleus of the daughter frequently contains excess energy and is unstable. Stability is usually achieved very quickly through the release of energy in the form of one or more gamma rays. The daughter nucleus decays from one energy state to another without changing its atomic weight or number.

Beta particles

Beta particles (β) are electrons or positrons which are spontaneously ejected from the nuclei of radioactive atoms during the decay process. These particles may either be positively (positron) or negatively (electron) charged.

The beta-minus decay can appear when the mass of the initial nucleus *M(A, Z)* is higher than the mass of the resulting nucleus more than the mass of one electron. The resulting nucleus has the same number of nucleons as the initial nucleus.

There is an optimum neutron/proton ratio for stability of the atom. If an element with nucleus has much more neutrons than protons, then it becomes unstable. Nuclides at the optimum ratio are stable. The further the neutron/proton ratio from the optimum, the less stable the nuclide and the more probable that a given atom will disintegrate within a specified time interval.

If the neutron/proton ratio exceeds the optimum, then beta-minus decay is probable. Beta-minus decay tends to relieve this departure from the optimum because, in essence, one of the neutrons in the nucleus is converted to a proton, reducing the neutron/proton ratio.

$n \rightarrow p + e^{-} + \text{antineutrino}$

Spontaneous decay of the neutron follows, with emission of the electron and antineutrino.

In terms of electric charge of nucleus, the change become for 1 unit larger.

The antineutrino has very little mass and is electrically neutral; therefore, it transmits little energy to the medium through which it travels. It does, however, carry off a variable part of the energy of the transformation. This helps to explain why beta particles are emitted from a given radionuclide with a spectrum of kinetic energies varying from zero up to a specific maximum energy *Emax* equal to difference between the initial and the final energy state of the nucleus.

The energy spectrum of the electrons of beta-minus decay are shown in Fig. 5, Te being the energy of beta particle. Fig. 6 shows the beta-minus decay of Cs-137.

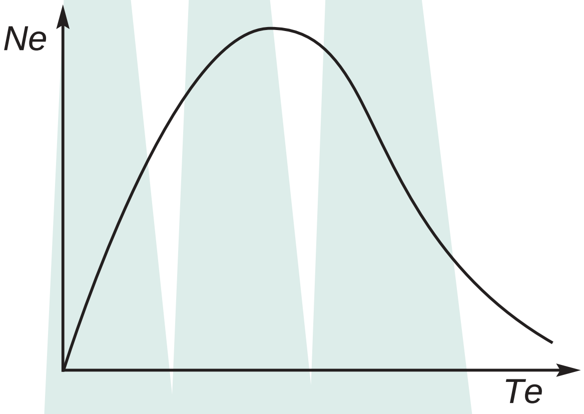


Fig. 5 **Energy spectrum of electrons of beta-minus decay**

Emission of the electron and antineutrino in Fig. 6 are shown as the arrow from ground state of *Cs-137* to the excited state of *Ba-137* (excitation energy of 661.6 *keV*). The maximum energy of the electron can be 514 *keV*. On average, 94% of all nucleus decays' occurs in this way, while another 6% decays with maximum energy of electrons equal to 1,176 *keV* to ground state nucleus of *Ba-137*. The nucleus of *Ba-137* in an excited state emits gamma rays with an energy of 661.6 *keV* and becomes the nucleus of *Ba-137* in a ground state.

Sometimes, at the time of radioactive beta decay, the excited state levels of the resulting nucleus cannot be filled. Fig. 7 represents beta-minus decay of *Sr-90*. As shown

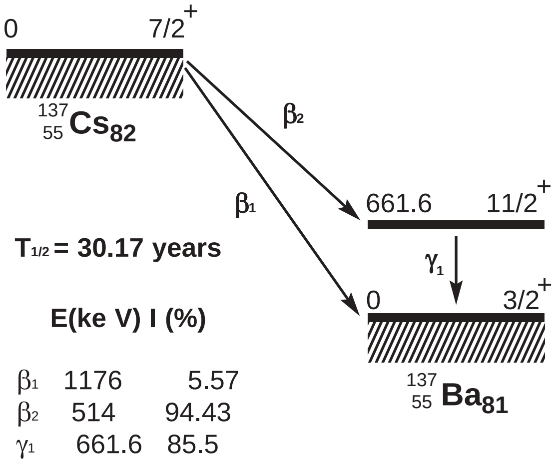


Fig. 6 **Beta-minus decay of Cs-137**

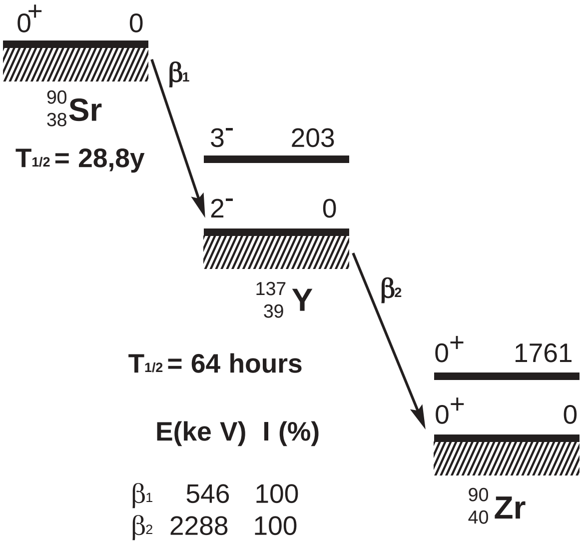


Fig. 7 **Beta-minus decay of Sr-90**

in Fig. 7, the *Sr-90* decay occurs with 100% probability to *Y-90* in ground state, and in this case there are no emission of gamma rays.

The beta-plus decay can appear when the mass of the initial nucleus *M(A, Z)* is higher than the mass of the resulting nucleus *M(A, Z-1)* more than the mass of one positron. The resulting nucleus has the same number of nucleons as the initial nucleus.

If the neutron/proton ratio is less than optimum, then beta-plus decay is probable. One of the protons in the nucleus is converted to a neutron, changing the neutron/proton ratio.

$p \rightarrow n + e^+ + \text{neutrino}$

Therefore, the nucleus undergoes spontaneously decay with emission of a positron and a neutrino.

In terms of nucleus electrical charge, the charge becomes lower for 1 unit.

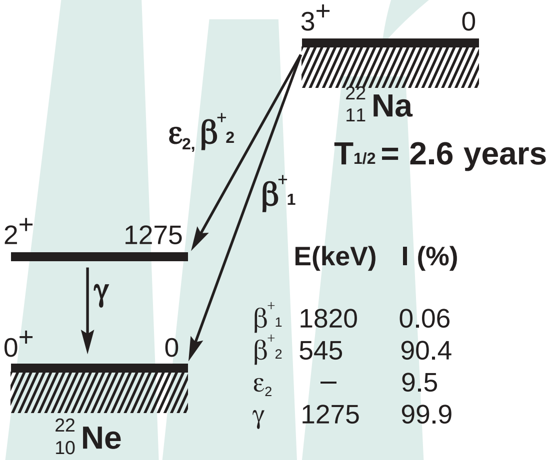


Fig. 8 **Beta-plus decay and electron capture of Na-22**

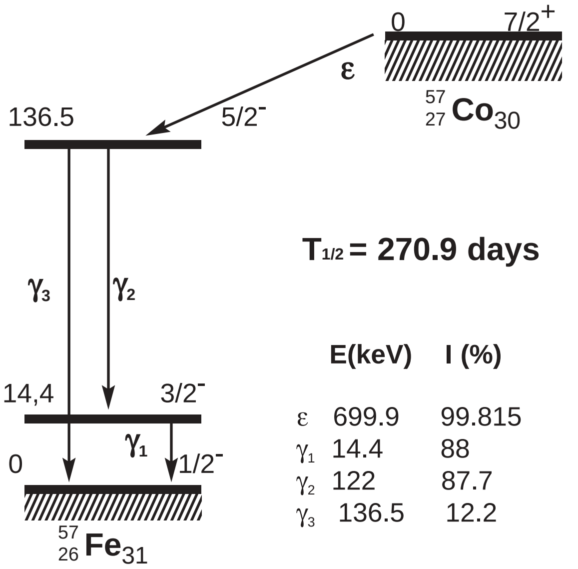


Fig. 9 **Electron capture process of Co-57**

Except for the electrical charge, the properties of the positrons are identical to electrons and they may be detected with the same methods.

Radionuclides with a less than optimum neutron/proton ratio may also decay by a process called *"electron capture"*. In this process, the parent nucleus may capture an orbital electron (usually neighbour to the nucleus) and subsequently emit an antineutrino and one or more photons, ridding of excess energy. For example, Fig. 8 shows beta-plus decay and electron capture of *Na-22* and Fig. 9 shows the electron capture process of *Co-57*.

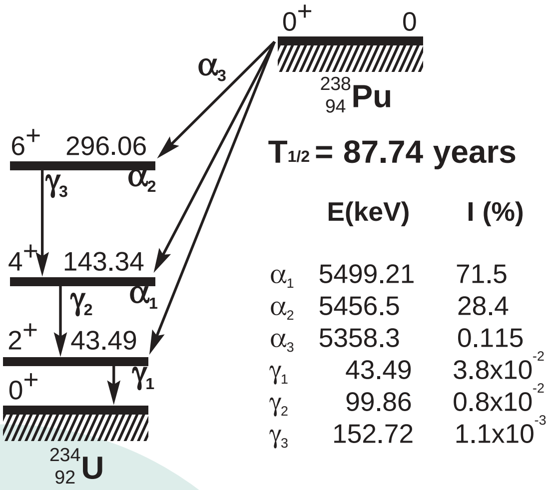
Alpha particles

An alpha particle *(α)* is essentially a helium nucleus without orbital electrons and is composed of two protons and two neutrons with a charge of plus two.

Alpha particles originate primarily from nuclear decay of a number of the radioactive elements with atomic mass numbers greater than 82.

Nearly all the energy liberated by this transformation is carried by the alpha particle as kinetic energy.

Alpha decay can appear when the mass of the initial nucleus M(A,Z) is higher than the mass of the resulting nucleus M(A-4,Z-2) more than the mass of one alpha particle. The charge is changed by -2 since in terms of electric charge and atomic mass the number is changed by -4. Fig. 10 represents the alpha decay process of Pu-238.



	E(keV)	I (%)
α_1	5499.21	71.5
α_2	5456.5	28.4
α_3	5358.3	0.115
γ_1	43.49	$3.8\text{x}10^{-2}$
γ_2	99.86	$0.8\text{x}10^{-2}$
γ_3	152.72	$1.1\text{x}10^{-3}$

Fig. 10 **Alpha decay process of Pu-238**

3.1.3 Nuclei transformation law and specific activity

Radioactivity is the result of the process in which the parent radionuclide undergoes spontaneous decay and forms a daughter radionuclide. The number of nuclear decays per unit time is proportional to the number of radioactive material atoms in a sample. The representation of radioactive decay law is as follows:

$$\frac{dN}{dt} = -\lambda \cdot N \tag{2}$$

where *N* is the number of radioactive atoms, *t* is time, and λ is the decay constant. The expression dN/dt is rate of the number of atoms changing in time. This equation is equivalent to:

$$N = N_0 \cdot \exp(-\lambda \cdot t) \tag{3}$$

where N_0 is the number of radioactive atoms in the initial moment of time *t=0*.

Radionuclide half-life *($T_{1/2}$)* is a value of time *t* in which the number of radioactive atoms decreased by a factor of two (when $N = ½ \cdot N_0$). From Eq. 3 it easy to see that:

$$T_{1/2} = \frac{\ln 2}{\lambda} \approx \frac{0.693}{\lambda} \tag{4}$$

The quantity of radioactive substance may be expressed as activity (amount of decays per unit time).

The Eq. 3 indicates that instantaneous change rate in the number of nuclear disintegration is the product of the decay constant λ and the number of atoms. Using the notation for activity A*, one can write:

$$A^* = \lambda \bullet N \qquad (5)$$

The unit of activity is Becquerel (*Bq*) equalling to one decay per second. The number of radioactive atoms N in a sample of specific radionuclide is given by:

$$N = (m \bullet N_A) / A \qquad (6)$$

where m is the mass of substance in grams, N_A is Avogadro's number (6.025×10^{23} mol^{-1}), and A is the atomic mass number of radionuclide.

The half-life of a radionuclide gives some immediate insight into its behaviour and prolongation of the hazard, which might be associated with it.

The conventional unit of radioactivity is *Curie* (*Ci*). The Curie was originally designated as the amount of radioactivity emitted by 1g of ^{226}Ra. This activity is approximately equal to 3.7×10^{10} *Bq*. It is important to note that the Becquerel and Curie units only specifies the number of nuclear disintegrations per second and does not specify amount or types of radiation emitted per unit time.

The exponential law of radioactive decay as given by Eq. 3 is valid only for the case when the number of radioactive nuclei decreases solely due to decay and there are no other sources of new radioactive nuclei creation. If not so, the law will be much more complicated.

3.2 Sources of radioactivity

3.2.1 Natural sources

Throughout the history of life on earth, organisms have continuously been exposed to cosmic rays, radionuclides produced by cosmic ray interactions in the atmosphere, and radiation from naturally occurring substances which are ubiquitously distributed in all living and nonliving components of the biosphere. It is clear that contemporary life forms have adjusted or are doing so to all features and limitations of the environment, including the natural radiation background.

Although higher levels of radiation are definitely harmful to organisms, some environmental radiation is important to life, as we know it. For example, background radiation has contributed, though we do not know how much, to the fundamental processes of chemical and biological evolution. Of clearer importance is the fact that the earth's heat content is principally provided and maintained by the heat of decay of primordial, naturally occurring radionuclides. Were it not for this, the earth would be a totally different place.

Cosmic rays

Radiation of extraterrestrial origin, which rains continuously upon the earth, is termed *"cosmic rays"*.

The fact that this highly penetrating radiation was impinging upon the earth from space, rather than emanating from the earth, was deduced from balloon experiments in which ionisation measurements were made at various altitudes from sea level to 9,000 metres It was found that the ionisation rate decreased for some 700 metres and from that point increased quite rapidly with elevation. The initial decrease could be explained by a decreased intensity of terrestrial gamma rays, while the increasing component was due to cosmic rays. The likely origin of cosmic rays is the almost infinite number of stars in the universe. Evidence for this is the increased cosmic ray intensity observed on earth following solar flares. However, it is clear that the sun is not normally a major contributor to the total cosmic flux since diurnal variations are very small.

Cosmic rays may be termed *“primary”* or *“secondary”*. Those, which have not yet interacted with matter in the earth’s atmosphere, lithosphere, or hydrosphere, are termed primary. These consist principally of protons (≈85%) and alpha particles (≈14%), with much smaller fluxes (<1%) of heavier nuclei. Secondary cosmic rays, which are produced by interactions of the primary rays and matter, consist largely of subatomic particles such as pions, muons, and electrons. At sea level, nearly all the observed cosmic radiation consists of secondary cosmic rays, with some 68% of the flux accounted for by muons and 30% by electrons. Less than 1% of the flux at sea level consists of protons.

Primary cosmic rays usually possess tremendous kinetic energy. Some particles having energies up to 10^{10} *GeV* (*1GeV* = 10^{9} *eV*) have been observed.

Cosmic ray intensity increases sharply with elevation until a maximum is reached at an altitude of about 20 km. From 20 km to the limit of the atmosphere (up to 50 km), the intensity decreases. This pattern is explained by increased production of secondaries resulting from the increasing atmospheric density as one move toward earth from an altitude of 50 km. At 20 km, most of the primaries have interacted and the decreasing intensity from a 20 km altitude to earth reflects the absorption of secondaries by the atmosphere, which is equivalent to some 10 metres of water.

Table 22 **Radionuclides produced from cosmic rays**

Radionuclide	Half-life	Atmospheric production rate (atoms/cm^{2}-sec)
^{10}Be	2.7×10^{6} year	4.5×10^{-2}
^{36}Cl	3.1×10^{5} year	1.1×10^{-3}
^{14}C	5568 year	1.8
^{32}Si	500 year	1.6×10^{-4}
^{3}H	12.3 year	0.25
^{22}Na	2.6 year	5.6×10^{-5}
^{35}S	88 day	1.4×10^{-3}
^{7}Be	53 day	8.1×10^{-2}
^{33}P	25 day	6.8×10^{-4}
^{32}P	14.3 day	8.1×10^{-4}
^{27}Na	15.1 hr	
^{38}S	2.9 hr	
^{39}Cl	55 min	1.6×10^{-3}
^{38}Cl	37 min	

Cosmic ray intensity is also related to latitude. At a given altitude, the cosmic flux increases from the equator to a latitude of 50 to 60°. The flux remains roughly constant from 50 to 60° to the poles. The shape of the earth's magnetic field and the energy distribution of primaries can explain the latitude effect. Magnetic lines of force extending beyond the atmosphere are generally parallel to the earth's surface at the equator, and perpendicular at the poles. Charged primary particles can easily penetrate the magnetic field when aligned with the lines of force. However, only the more energetic primaries can penetrate the field when not aligned. From the poles to 60 degrees, virtually all the primaries reach the earth's atmosphere, whereas at the equator, only those primaries exceeding about 15 *GeV* penetrate the magnetic shield.

A considerable number of radionuclides are continuously produced in the atmosphere by cosmic ray interactions with matter (Table 22). Most of these radionuclides are produced as fragments, but some are formed by activation of stable atoms with neutrons or muons. The natural production of radionuclides in the atmosphere shows elevational and latitudinal patterns similar to those of cosmic ray intensities. About 70% of the fragmentation-produced nuclides arise in the stratosphere, while about 30% are formed in the troposphere.

With the possible exceptions of *H-3* and *C-14*, the radionuclides in Table 22 are normally found in very minute concentrations. Tritium is diluted and mixed with the earth's water and *H-2* gas reservoirs, while *C-14* combines with oxygen to form CO_2, which mixes with the atmospheric CO_2 pool. Carbon-14 enters plants through the process of photosynthesis. Nuclear explosions can also produce a number of the radionuclides listed in Table 22, including *H-3*, *C-14*, *Be-7*, *Na-22* and *P-32*.

Terrestrial radiation

Radionuclides, which appeared at the time of formation of the earth, are termed "primordial". Of the many radionuclides that must have been formed with the earth, only a few have half-lives sufficiently long to explain their current existence. If the earth were formed about $6x10^9$ years ago, a primordial radionuclide would need a half-life of at least 10^8 years to still be present in measurable quantities. Of the primordial radionuclides that are still detectable, three are of overwhelming significance. These are *K-40*, *U-238* and *Th-232*. Uranium and thorium each initiate a chain of radioactive progeny, which are nearly always found in the presence of the parent nuclides (Table 23). Although many of the daughter radionuclides are short-lived, they are distributed in the environment because they are continually being forming from long-lived precursors.

Other primordial long-lived radionuclides which occur in nature are *Rb-87*, *La-138*, *Ce-142*, *Sm-147*, *Lu-176* etc. Those radionuclides are generally in very low concentrations.

The main reservoir of natural radioactivity is the lithosphere. However, considerable variation in radioactivity exists within the lithosphere. Some variations appear associated with specific types of formations and certain minerals, while other variations appear to be strictly regional, with little correlation to types of rocks and minerals.

The distribution of the primordial radionuclides and their progeny in natural ecosystems is influenced by many factors, including chemical properties of the nuclides, physical factors of the ecosystem, and physiological and ecological attributes of the biota. A simple compartment diagram of a terrestrial ecosystem, showing pathways along which some of the more abundant natural radionuclides have been shown to move, is given in Fig. 11.

Weathering of bedrock, the main reservoir of the primordial radionuclides, releases *U*, *Th*, and *K* to the soil. Progeny of *U* and *Th* also take part in this transfer. From soil, *K*, *Ra*, small amounts of *U* and extremely small quantities of *Th* are taken up by plants. The plants utilise potassium-40 in the same manner as it uses the essential element, stable *K*. Radium, an

Table 23 **Primary decay schemes of U-238 and Th-232**

Uranium-238			Thoruium-232		
Radionuclide	Half-life	Radiation	Radionuclide	Half-life	Radiation
^{238}U	4.5 x 10^{9} year	α, γ	^{232}Th	1.4x10^{10} year	α, γ
^{234}Th	24 day	β, γ	^{228}Ra	6.7 year	γ, β
^{234}Pa	1.2 min	β, γ	^{228}Ac	6.1 hr	γ, β
^{234}U	2.5 x 10^{5} year	α, γ	^{228}Th	1.9 year	α, γ
^{230}Th	8 x 10^{4} year	α, γ	^{224}Ra	3.6 day	α, γ
^{226}Ra	1620 year	α, γ	^{220}Rn	55 sec	α, γ
^{222}Rn	3.8 day	α, γ	^{216}Po	0.16 sec	α, β
^{218}Po*	3.1 min	α, β	^{212}Pb	11 hr	γ, β
^{214}Pb	27 min	β, γ	^{212}Bi	61 min	α, γ, β
^{214}Bi*	20 min	α, γ, β	^{212}Po	3x10^{-7} sec	α
^{214}Po	1.6 x 10^{-4} sec	α	^{208}Pb	Stable	None
^{210}Pb	19 year	β, γ			
^{210}Bi*	5 day	α, γ, β			
^{210}Po	138 day	α, γ			
^{206}Pb	Stable	None			

* Alternate, less frequent branching decays not shown

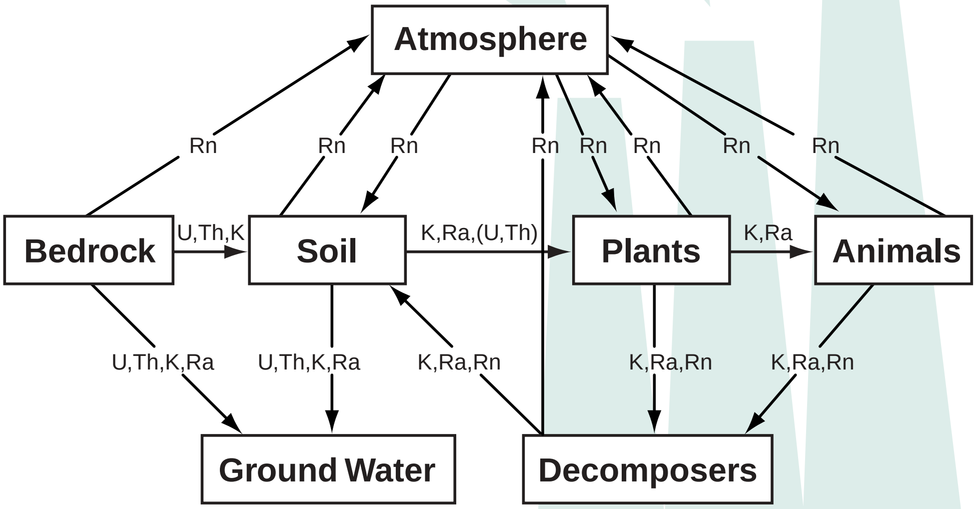


Fig. 11 **Major pathways of primordial radionuclides and important progeny in terrestrial ecosystem**

/Symbols: U = uranium isotopes, Th = thorium isotopes, Ra = radium isotopes, Rn = radon isotopes or progeny of radon decay/

important longer-lived progeny of *U-238*, is utilised by the plant, not because it is an isotope of an essential element, but because it is chemically similar to calcium, which is essential. The uptake of *U* and *Th* by plants is usually small or negligible since these radionuclides normally are relatively insoluble.

Radon

The most important of all sources of natural radiation is a tasteless, odourless, invisible gas about eight times heavier then air, called radon. It has two main forms – Radon-222, one of the radionuclides in the sequence formed by the decay of *U-238*, and Radon-220, produced during the decay series of *Th-232*.

Bedrock, soil, plants, animals, and decomposer compartments all release radon to the atmosphere. Radon is the decay product of radium and is produced in any material containing radium. Since radon is one of the inert gases, it can escape from surfaces which are in contact with the atmosphere. The amount of radon, which emanates from a given mass of rock depends upon the quantity of radium present and upon the amount of surface area presented by the mass. The more finely broken a given mass of rock, the more radon it can release. The concentration of radon in the air adjacent to radium-bearing material also depends upon the rate of fresh air movement into the space in question. In basements, caves, and mine shafts that have poor air circulation, radon concentrations can build up to very significant levels. Efficient ventilation in mines is often necessary to maintain radon concentrations below those which would be hazardous for workers.

Radon decays quite rapidly to form a series of daughter radionuclides (Table 23). Once formed in the atmosphere, the progeny of radon attach to small dust particles, which are subject to deposition on soil and plants and to inhalation by animals. Rainfall is particularly efficient in scrubbing radon daughters from the atmosphere, but impacting and sedimentation of aerosol particles also contribute to deposition.

In temperate parts of the world the concentrations of radon indoors, on average, are about 5 to 10 times higher than they are outdoors. Radon concentrates in indoor air when buildings are, by and large, closed spaces.

3.2.2 Man-made sources

Over the last few decades' man has "artificially" produced several hundred radionuclides. And he has learned to use the power of the atom for a wide variety of purposes, from medicine to weapons, from the production of energy to the detection of fires, from illuminating watches to prospecting for minerals.

Individual effects from man-made sources of radiation vary greatly. Most people receive a relatively small amount of artificial radiation; but a few get many thousand times the amount they receive from natural sources.

This variability is generally greater for man-made sources than for natural ones. Most man-made sources can be controlled more readily than most natural ones. Exposure to external radiation, due to fallout from past nuclear explosions, for example, is almost as inescapable and uncontrollable as that due to cosmic rays from beyond the atmosphere or to radiation from out of the earth itself.

Medical sources

In industrial and medical applications, typically only single radionuclides are involved, thus simplifying identification of leakage pathways from encapsulation, from radioactive tracer tests and for the disposal process. However, even there one may encounter more than one in the source material because of the reactions.

The use of radioisotopes in medicine is widespread and may potentially have significant radiological impact. These applications can be classified as:

- diagnostic uses
- therapy
- analytical procedures
- pacemakers and similar portable sources

Both sealed sources and a wide variety of radioactive tracers are used in diagnostic applications; medical institutions usually distinguish carefully between these two applications as radiology and nuclear medicine, respectively. X-ray fluoroscopy is a well-known diagnostic radiographic procedure, typically employing an X-ray tube as a source. However, there is a variety of isotopic source applications for medical radiography, employing gamma sources, beta sources and, experimentally, neutron sources for image formation under conditions where X-ray units would be inconvenient, inappropriate, or might cause operational hazards. Environmentally, radiographic sources are negligible as source terms as long as they remain accountable and are disposed of properly. In this respect, the history of radium sources, radon needles, and radium-containing luminescent compounds has not been encouraging.

Occupational exposures from work on radium-containing watch dials and tritiated luminous signs have been substantial and radium-contaminated rooms and buildings, many of them dating to the early decades of this century, are being found from time to time all over the world.

The emergence of ^{252}Cf as a portable neutron source has made neutron radiography more widely available, although generally the method is still heavily dependent on nuclear reactors as sources. There are also a number of routine applications for ^{90}Sr or ^{147}Pm-based *bremsstrahlung* sources.

The major potential environmental impact arises from the use of radioactive tracers in nuclear medicine, a field that has grown enormously in recent years. Nuclear medicine exposures can be classified as:

- exposure of the patient
- exposure of hospital personnel
- exposure during transport of radioactive pharmaceuticals
- exposure during manufacture
- exposure from radioactive waste

Developments in recent years have tended to reduce patient exposure through the introduction of short-lived isotopes of higher specific activity and the use of more highly localized preparations. The shorter half-life also simplifies the impact of radioactive waste, since most of the longer-lived activity is usually eliminated through the kidneys into the sanitary waste system. The flow of radioisotopes in a nuclear medicine department of a hospital is shown in Fig. 12.

Presumably, the environmental impact, via the sewers, of any excreted material is the same for inpatients or outpatients. Although most of the excreted radioactivity is likely to be short-lived, the aggregate environmental impact from this source probably greatly exceeds that of all nuclear power plants from routine effluents.

Most often radionuclides used in medicine are:

- ^{99m}Tc bone marrow scan, brain scan, cerebral blood scan, heart scan, liver scan, lung can, thyroid scan, placental localisation

- ^{131}I	blood volume, liver scan, placental localisation, thyroid scan, and thyroid therapy
- ^{51}Cr	red blood cell survival or sequestration, blood volume
- ^{57}Co	Schilling test
- ^{32}P	bone metastases

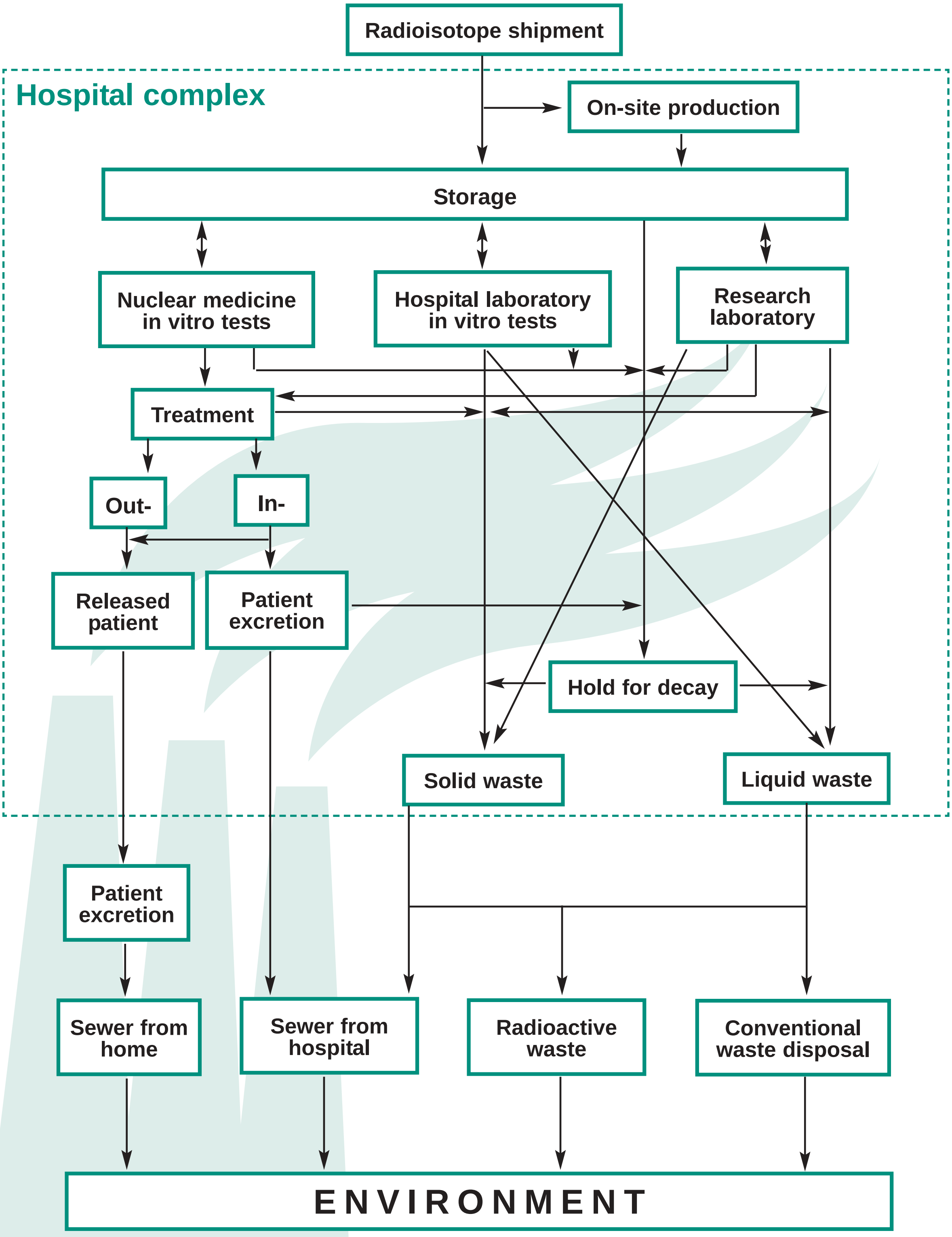


Fig. 12 **Hospital radioisotope flow diagram**

The widespread use of radioimmunoassay procedures, radioactive urine analyses, and other research methods employing labelled organic compounds has greatly increased the use of liquid scintillation detection units. The organic phosphor solutions, usually based on toluene or xylene, constitute a rather large volume of liquid organic contaminated waste that must be disposed of.

Disposal in liquid form is potentially hazardous and environmentally no longer acceptable. For that reason, incineration is preferred, but there are still a number of technical problems to be solved before incineration can be considered an acceptable alternative to the present methods of disposal. Since most of the activity involved is long-lived ^{3}H or ^{14}C, both readily diluted in the environment, the impact is ethical and regulatory in nature rather than a major localised source of contamination. However, again, the cumulative activities involved may be substantial.

The final medical use of radionuclides to be covered here concerns the use of plutonium batteries to power cardiac pacemakers. Thousands of people are alive today because pacemakers help their hearts to function. Sealed sources of ^{238}Pu, typically ^{4}Ci (150 *GBq*) in activity, are surgically implanted in the patients.

Industrial sources

Radioisotopes are much more widely used in industry than is generally recognized and represent a significant component in the man-made radiation environment. The principal applications include industrial radiography, radiation gauging, smoke detectors and self-luminous materials. Because most of these applications entail the utilisation of encapsulated sources, radiation exposures would be expected to occur mainly externally during shipment, transfer, maintenance, and disposal.

In the past decade, radiation exposures in research and industrial applications were roughly half those due to medical occupational exposure; hence, their contribution to the direct

Table 24 **Typical uses of radionuclides in industry**

Application	Radionuclides	Typical source strengths
Encapsulated sources		
Industrial radiography	^{192}Ir, ^{137}Cs, ^{170}Tm, ^{60}Co	10-100 Ci (0.4-4TBq)
Borehole logging	^{137}Cs, ^{60}Co Pu-Be, Am-Be ^{252}Cf	10 mCi-2 Ci (0.4-70GBq) 50 mCi-20 Ci (1.9-700GBq) 100 µCi (4MBq)
Radiation gauges, automatic weighing equipment	^{90}Sr, ^{147}Pm, ^{144}Ce, ^{137}Cs, ^{60}Co	5-200 mCi (0.2-7GBq)
Smoke detectors	^{241}Am	5 µCi (200 kBq)
Luminous signs	^{3}H	0.5 Ci (20 GBq)
Mossbauer analysis	^{57}Fe, ^{57}Co	2-50 µCi (0.4 MBq)
Tracer application		
Hydrological tracers	^{3}H ^{82}Br	1-100 Ci (4 TBq) 10-100 mCi (-4 GBq)
Reservoir engineering	^{85}Kr	200 mCi (7 GBq)

population dose is substantial. Table 24 lists the principal radionuclides involved and typical applications.

In terms of subsequent movement through the environment, such encapsulated sources obviously do not represent a significant source term. They contribute to specific assessment areas, such as transport and waste disposal, and occasionally cause alarm when one is lost or misdirected or even placed in a municipal garbage dump by mistake.

Sealed sources for industrial use typically are shipped and installed in the form of doubly encapsulated disks or cylinders. In most cases, the capsule material is stainless steel, ring-welded, and required to be leak-tested at regular intervals.

Disposal of industrial sources may pose a problem. There is a certain second-hand value associated with cobalt therapy sources and some longer-lived radiography sources. Shorter-lived sources may be stored and allowed to decay, but even then they must be properly accounted for, and the residual active material must be disposed of at a licensed facility. Stronger sources similarly must be shipped to a licensed facility for disposal; finding such a facility is becoming more and more difficult under present conditions.

Increasing attention is being paid to the safe decommissioning and decontamination of industrial sites where radioactive materials have been handled in the past. Most are plants built for processing nuclear materials in the early days, but increasingly other industries have become involved, such as plants making self-luminous tritium-containing signs.

A special problem may exist for long-lived low-level sources that are widely distributed such as ^{241}Am alpha sources used in smoke detectors. Individually they pose no hazard, and it would require a rather artificial scenario for them to be reconsolidating at a future time in sufficient amounts to pose a problem.

Nuclear explosions

For the last 40 years, everyone has been exposed to radiation due to fallout from nuclear weapons. Almost all is the result of atmospheric nuclear explosions carried out to test nuclear weapons. This testing reached two peaks: the first between 1954 and 1958 and the second, greater one, in 1961 and 1962.

In 1963 three countries (the USSR, the United States and the United Kingdom) signed the Partial Test Ban Treaty, undertaking not to test nuclear weapon in the atmosphere, oceans and outer space. Over next two decades France and China conducted a series of smaller tests, but they, too, stopped after 1980 and there have been no atmospheric tests since that time. Underground tests are still being carried out, but they generally give rise to virtually no fall-out.

Some of the radioactive debris from atmospheric tests lands relatively close to the site of explosions. Some stays in the troposphere, the lowest layer of the atmosphere, and is carried by the wind around the world at much the same latitude. As it travels it gradually falls to earth, remaining in the air about one month. But most is pushed into the stratosphere, the next layer of the atmosphere (10 to 50 km up) where it stays for many months, and whence it slowly descends all over the earth.

These various types of fallout contain several hundred different radionuclides, but only a few contribute much to human exposure, as most are produced in very small amounts or decay quickly. Those few, in declining order of importance, are carbon-14, caesium-137, zirconium-95 and stronium-90.

Zirconium-95, which has a half-life of 64 days, is already completely decayed. Caesium-137 and stronium-90, with half-lives of about 30 years, are still present, but containing less than half their initial amounts. Only carbon-14, with a half-life of 5,730 years, will stay active far into the future.

Nuclear power

The production of nuclear power is the most controversial of all the man-made sources of radiation, yet it makes a very small contribution to human exposure. In normal operation, most nuclear facilities emit very little radiation into the environment.

By the May 2001 there were 438 nuclear power reactors in operation in 25 countries, worldwide. These power stations are just part of the nuclear fuel cycle. This starts with the mining and milling of uranium ore and proceeds to the making of nuclear fuel. After use in power stations the irradiated fuel is sometimes “reprocessed” to recover uranium and plutonium. Eventually the cycle will end with the disposal of nuclear wastes. At each stage in this cycle radioactive materials can be released.

About half of the world’s uranium ore comes from open cast mines and half from underground ones. It is then taken to mills, usually nearby, for reprocessing. Mills produce large amount of waste or “tailings” – totally hundreds of millions tonnes. The wastes remain radioactive for millions of years after mills cease operation, albeit resulting in radiation exposure that is a very small fraction of the natural background.

After leaving the mills, uranium is turned into fuel by further processing and purification and, usually, by passing through an enrichment plant. These processes give rise to both airborne and liquid discharges, but effects are very much smaller than from other parts of fuel cycle.

The quantities of different types of radioactive materials released from these reactors vary widely, not only from type to types, but even between different designs within these types, and even between reactors of the same design. They also vary from year to year for the same reactor, partly because the amount of maintenance work differs each year. Materials that can be released into the environment are presented in Fig. 13.

3.3 Interaction of radiation with matter

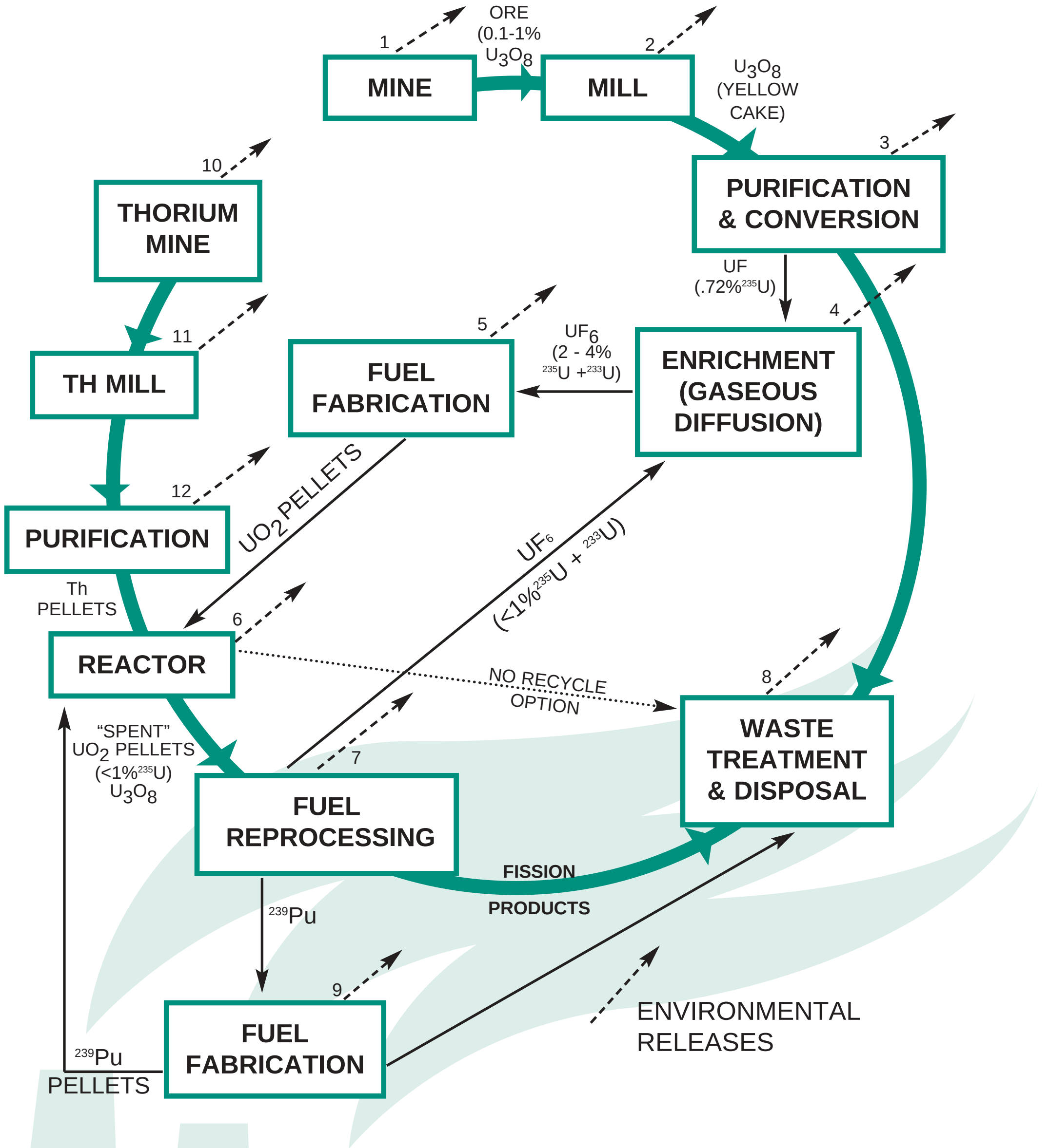
The detection, characterisation and effects of radiation are almost entirely dependent upon their interaction with matter.

Types of radiation are direct ionising radiation and indirect ionising radiation. The flows of charged particles, such as alpha particles, beta particles, electrons, are phenomena of direct ionising radiation, because though coulomb interaction with matter it directly cause ionisation and excitation of atoms. Indirect ionising radiation (neutrons, γ-quantums) is radiation of particles or photons, which have no charge and during interaction with matter can transfer energy to charged particles, nuclei and atom electrons due to electromagnetic or nuclear interaction.

3.3.1 Alpha particles absorption

Because alpha particles are comparatively heavy and have a double charge, they react strongly with matter, producing large numbers of ions per unit length of their path. As a result, they are not very penetrating. For example, a 5 *MeV* alpha particle will only travel about 3.6 cm in the air and will not penetrate an ordinary piece of paper. For the other materials the average travel distance with respect to air is approximately inversely proportional to the respective densities of each material. A *5 MeV* alpha particle will only travel about 4 μm in mammal tissue.

Alpha particles can interact with either nuclei or orbital electrons in any absorbing medium such as air, water, tissue or metal. An alpha particle passing in the vicinity of a nucleus may be deflected with no change in energy (Rutherford scattering), deflected with a small change in energy (this process is negligible for alphas) or absorbed by the nucleus, causing nuclear transformation.



1 - U, Th, Ra, Rn
2 - Th, Ra, Rn, (U) + PROCESSING CHEMICALS
3 - NO_2, HF, CaF, (UF_6), (^{234}Th)
4 - HEAT, COAL FIRED EMISSIONS, (UF_6)
5 - CHEMICALS, F_2, HNO_3
6 - ^{3}H, ^{85}Kr, ^{133}Xe, ^{37}Ar, ^{131}I, OTHER FISSION PRODUCTS (FP), HEAT
7 - ^{85}Kr, ^{3}H, ^{131}I, ^{129}I, OTHER FP, TRANSURANICS, MANY CHEMICALS
8 - LONG-LIVED FP, TRANSURANICS
9 - CHEMICALS, (Pu)
10 - Th, Ra, Rn,
11 - Ra, Rn, (Th)+ PROCESSING CHEMICALS
12 - CHEMICALS, Th

Fig. 13 **Basic elements and options within the nuclear fuel cycle, showing the kinds of materials that can be released to the environment**

The most probable processes involved in the absorption of alphas, however, are ionisation and excitation of orbital electrons. Ionisation occurs whenever the alpha particle is sufficiently close to the electron to pull it out from its orbit through coulomb attraction. Each time this occurs, the alpha loses kinetic energy and is thus slowed. The alpha also loses kinetic energy by exciting orbital electrons with interactions that are insufficient to cause ionisation. As it becomes slowed, the alpha has a tendency to cause ionisation at an increasing rate. As the alpha nears the end of its track, its rate of ionisation peaks and, within a very short distance, it stops, collects two electrons and becomes a helium atom.

Since alphas have a low penetration ability, they themselves are usually not hazardous, unless the alpha-emitting nuclide is deposited within the tissues of an organism. When internally deposited, however, alpha particles are often more damaging than most other types of particles because comparatively large amounts of energy are deposited within a very small volume of tissue.

3.3.2 Beta particles absorption

Beta particles can interact with electrons as well as nuclei in the medium through which they are travelling. Beta particles passing near a nucleus will be deflected be the coulomb forces and a loss in kinetic energy of the beta may or may not occur (*Rutherford scattering*). In the case where energy is lost by the beta, X-rays are produced. The probability of occurrence of either process increases as the atomic mass number of the absorbing medium increases.

Of greater significance are the interactions of beta particles with orbital electrons. Coulomb repulsion between beta and electron frequently results in ionisation. In the ionisation process, the beta loses an amount of energy equal to the kinetic energy of the electron, plus the energy used to free it from the atom. A beta particle may produce 50 to 150 ion pairs per centimetre of air before its kinetic energy is completely dissipated. As mentioned earlier, characteristic X-rays are emitted as the vacant electron orbits are refilled with other electrons. Beta particles also cause excitation of orbital electrons, which in turn leads to the emission of ultraviolet photons.

The ultimate fate of a beta particle depends upon its charge. A negatively charged beta particle, after its kinetic energy has been spent, either combines with a positively charged ion, or becomes a *“free electron”*. Positrons, however, have a different fate. In spite of the fact that they dissipate their kinetic energy just like beta particles through ionisation and excitation, they cannot exist at rest in the vicinity of electrons. When a positron has been slowed sufficiently, it will be attracted to the opposite charge of an electron. When the electron and positron collide, they are both annihilated and an amount of energy equal to the sum of the particle masses is released in the form of two photons. These photons are referred to as *“annihilation radiation”*. Both annihilation photons carry energy of 0.511 *MeV*, which is equivalent to the rest mass of the electron or the positron. Because of this phenomenon, 0.511 *MeV* photons often provide a convenient means for measurement of positron-emitting radionuclides.

Like alpha particles, betas have a characteristic average travelling distance (range) through matter that is dependent upon their initial kinetic energy. Beta particle range may be expressed as distance travelled in a certain medium. For example, 2 *MeV* beta particle will travel up to 9 metres and about 10 mm in water.

3.3.3 X-and gamma ray interaction

The interaction of photons with matter involves several distinct processes. The relative importance and efficiency of each process is strongly dependent upon the energy of the photons and upon the density and atomic number of the absorbing medium. The authors shall first consider the general case of photon attenuation and then discuss some of the important processes separately.

Raleigh scattering

When a photon encounters an orbital electron, it may or may not impart some energy to it. If the photon energy is less than the binding energy of the electron, the photon may be deflected with no energy transfer. This process is called Rayleigh scattering and is most probable for very low-energy photons.

Compton effect

The Compton effect is usually the predominant type of interaction for medium energy photons (0.3 to 3 *MeV*). In this process the photon interacts with an electron sufficiently to eject it from orbit, yet the photon retains a portion of its original energy and continues in a new direction. Thus, the Compton effect has an absorption component and scattering component. The amount of energy lost by the photon can be related to the angle at which the scattered photon travels relative to the original direction of travel.

The scattered photon will interact again, but since its energy has decreased, it becomes more probable that it will enter into a photoelectric or Rayleigh interaction. The free electron produced by the Compton process may be quite energetic and behave like a beta particle of similar energy, producing secondary ionisation and excitation before coming to rest.

Photoelectric absorption

The most probable fate of a photon having energy slightly higher than the binding energy of an encountered electron is photoelectric absorption. In this process, the photon transfers all of its energy to the electron and its own existence terminates. The electron will escape its orbit with a kinetic energy equal to the difference between the photon energy and its own binding energy. Photoelectric absorption is most important for photons below 0.1 *MeV* if the absorbing medium is water or biological tissue. However, in high Z (atomic mass number) materials such as lead, this process is relatively important for photons up to about 1 *MeV*.

As with ionisation produced by any process, secondary radiation are initiated, in this case, by the photoelectron which may have sufficient energy to produce additional ionisation and excitation of orbital electrons. Also, filling of the vacancy left by the photoelectron results in characteristic X-rays.

Pair production

Photons of energies greater than 1.022 *MeV*, under the influence of the electromagnetic field of a nucleus, may be converted into electron and positron. At least 1.022 *MeV* are required because the energy equivalent of the rest mass of the electron and positron is 0.511 *MeV* each. Pair production is not very probable, however, until the photon energy exceeds about 5 *MeV*. The available kinetic energy to be shared by the electron and the positron, is the photon energy minus 1.022 *MeV*, or that energy needed to create the pair. The probability of pair production increases with Z of the absorber and with the photon energy.

Relative importance of photon attenuation processes

The various processes of photon attenuation can now be considered by examining the effects of photon energy and atomic mass number of the absorber on their relative importance (Fig. 14). The lines in the figure indicate the values of the photon energy and Z where the probabilities of occurrence of two major processes are equal.

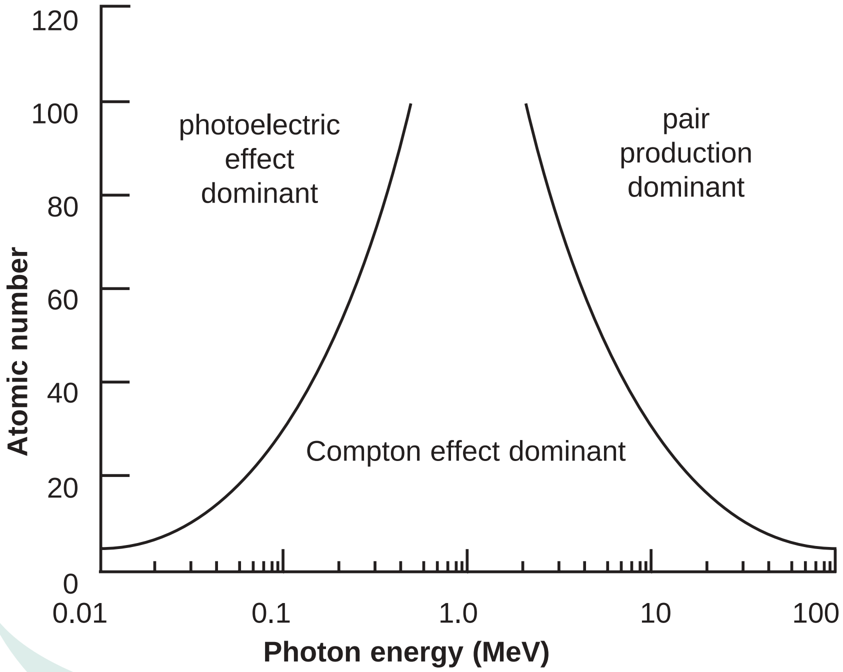


Fig. 14 **Effects of photon energy and atomic mass number of absorbing medium on dominant type of photon attenuation processes**

3.3.4 Neutrons

As mentioned above, neutrons affect living matter by the process of moderation. A high-energy neutron encountering biological material is apt to collide with a proton with sufficient force to dislodge the proton from the molecule which held it. The proton (normally called the "recoil proton") may then have sufficient energy to travel some distance in the tissue causing secondary damage through ionisation and excitation of molecules along its path.

3.4 Radiation identification and detection

Radiation monitoring instrumentation can be sub-divided into installed, transportable, portable, personal and laboratory equipment (Fig. 15). Installed, transportable and portable instruments can be further sub-divided into radiation monitoring equipment and contamination monitoring equipment. This is illustrated in Fig. 15.

3.4.1 Radiation monitoring equipment

Radiation monitoring equipment measures dose rate and/or dose. Beta/gamma dose rate meters are generally calibrated against a reference gamma source and will generally over-read beta dose rates. Beta/gamma dose rate meters generally have a window to enable beta radiation to enter the detector. With the window open the instrument detects beta and gamma radiation; with the window closed the instrument detects gamma radiation only. Such instruments may or may not be sufficiently robust for fieldwork. Care must be taken to avoid puncturing the window. Gamma dose rate meters with no thin window are more robust but are unsuitable for beta, low energy gamma and X-ray measurements. Beta/gamma dose rate meters may be sub-divided into low or environmental level, medium level and high level with the following dose rate ranges being applicable.

• Low (environmental)	0.05 µSv/h	–	100 µSv/h
• Medium	10 µSv/h	–	10 mSv/h
• High range	1 mSv/h	–	10 Sv/h

The high range instruments are often provided with a telescopic detector probe to maximize the distance of the operator from the source. In planning for an accident response it is important to have instruments that are capable of measuring in the desired range possible in accident conditions. For transport accidents low to medium instruments may be all that is needed. For major accidents involving highly radioactive sources medium to high range instruments are needed. For portable equipment an audio response is also desirable. If high ambient noise levels can be expected, such as heavy machinery or heavy traffic, earphones may be appropriate to assist the operator in locating discrete dose rate maximums. Installed dose rate instruments would generally have a set local audible alarm and warning lights and may also have readings and alarms relayed to a central monitoring control point.

Portable instruments may have digital or analogue scales. For digital readouts care must be taken with auto ranging equipment that changes from microsieverts per hour to millisieverts per hour. The scale must also be legible in bright sunlight and in heavy rain. The meter response time should be sufficient to enable the operator to take a reading without undue delay in waiting for the reading to settle around a particular value. For analogue instruments the scales may be logarithmic, quasi-logarithmic or linear. For logarithmic scales the operator will require training in reading the scale to ensure correct reporting of the reading. Linear scaled instruments are often provided with a range switch, typically *x1*, *x10*, *and x100*. Such instruments should be calibrated for each range to two-thirds full-scale deflection. Some instruments may have more than one detector, one for medium range, say, and one for high range. Such instruments should be calibrated for both detectors.

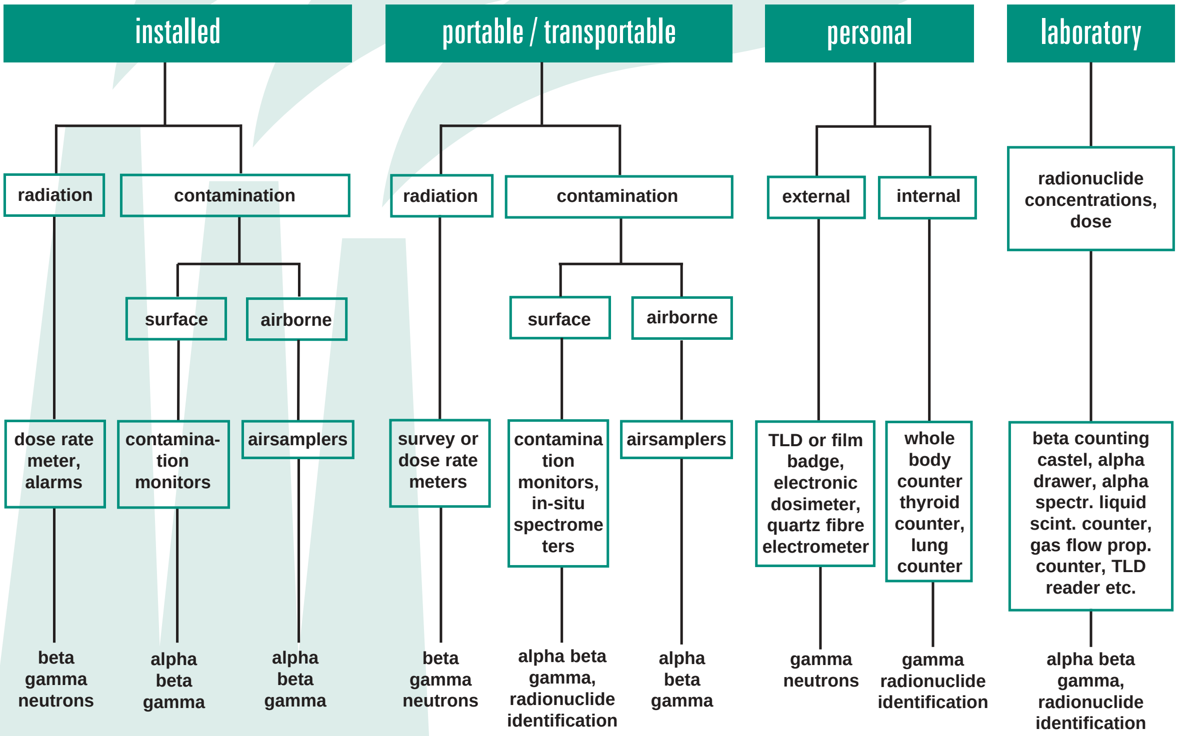


Fig. 15 **Radiation monitoring instrument types**

3.4.2 Contamination monitors

Contamination monitors may be sub-divided into those for measuring surface contamination and those for measuring air contamination. Surface contamination monitors are generally referred to as contamination monitors. Installed instruments such as hand and clothing monitors are located at barriers to contamination-controlled areas. In an accident temporary contamination control zones may be established in which all personnel, vehicles and equipment entering the area will be checked for contamination on leaving the area. Portable contamination monitors are used to check surface contamination arising from spillage of solid or liquid sources, contamination spread from physical handling of unsealed sources, and fall out from radioactive material in the air. They are also used to check the skin and clothing of persons, contamination of workbenches, floors, walls, machines, etc.

It is important to select the most appropriate contamination monitor for the type and energy of the radiation (alpha, beta or gamma) to be measured. Alpha radiation is usually detected with an instrument utilizing a zinc sulphide phosphor as a scintilator and a photomultiplier tube to amplify the signal which is then registered on an appropriate rate meter calibrated in counts per second (cps) or counts per minute (*cpm*) for specific alpha sources. Silicon semiconductor detectors and thin window Geiger-Muller (GM) detectors may also be utilised. In monitoring for alpha contamination, because of the short range of alpha radiation in the air, it is important to monitor close to the surface without touching the surface (to avoid contaminating the instrument) and to avoid puncturing the thin window of the detector. If surfaces are wet, alpha radiation will be difficult to detect due to the shielding provided by the water. If checking samples for alpha contamination with a portable contamination monitor the surface should be dry.

The most common type of beta/gamma contamination monitor utilises a Geiger detector. This is generally robust and gives a well-amplified signal but does not discriminate different gamma energies. Scintillation detectors such as plastic phosphors and solid crystals such as sodium iodide are also utilised for beta/gamma contamination monitoring. For low energy beta and gamma radiation thin window detectors are required. For moderate to high-energy betas more robust instrument with a thicker window may be utilised. Such instruments are usually provided with an end cap or shutter, which when open the instrument detects both beta and gamma radiation and when closed detects gamma radiation only. Some contamination monitors are provided with interchangeable probes. It is important that the voltage settings and calibration settings for the instrument are adjusted correctly for each type of probe. The rate meter may have a digital or analogue read-out and the comments made earlier when discussing dose rate meters comparing the use of analogue and digital scales are equally applicable here. An audio response is an essential adjunct for a contamination monitor as this enables the operator to focus his or her attention on where the probe or instrument is, rather than continuously watching the meter reading. Meter readings are taken in conjunction with audio response. Headphones may be of use, to enable the operator to clearly hear the instrument audio response in a noisy environment or for silent operation in the vicinity of members of the public to avoid unnecessary concern. It is important that the selected contamination monitor is appropriately calibrated for the radionuclides to be monitored in a geometry that reflects the measurement conditions. Gamma-only contamination monitors utilizing scintillation detectors, proportional counters, ionisation chamber detectors and GM detectors are also available. In selecting the most suitable instrument for field contamination monitoring in accident situations attention should be given to the ruggedised nature of the instrument, the use of readily available batteries that are easily changed in the field and simplicity of use. There are many sophisticated contamination monitors available in the market. Skilled operators should only use such instruments. For general purpose measurements less sophisticated instruments are preferable.

3.4.3 Air sampler

An air sampler consists of a pump which operates at a known or specified flow rate for a timed sampling period and which draws air through a suitable filter medium, which is subsequently analysed for the contaminant in question. The activity on the filter is assessed in *Bq* or *kBq* and knowing the volume of air sampled, results are given in *Bq*/m^3 or *kBq/*m^3. Installed air samplers exist within nuclear facilities to routinely monitor air contamination levels and give warning through audible and visual alarms if levels become abnormally elevated. Installed air samplers may also be placed at environmental locations to give an indication of air contamination levels at those locations. Transportable air samplers such as high volume air samplers, operated by portable electrical generators may be set up in locations of interest. Portable air samplers with an operating voltage of 12 V are useful in a field-sampling situation. Here the sampler can be connected to the battery of the monitoring vehicle either directly using crocodile clips, or indirectly via the vehicle cigarette lighter. Portable air samplers work at flow rates in the tens of litres per minute. They may either utilise a critical orifice to restrict the flow to a certain flow rate or have incorporated in them an adjustable flow rate rotameter, or their flow rate may be pre-calibrated. Care should be taken if there is a heavy dust loading on the filter as this may restrict the flow rate. In such cases the flow rate rotameter should be checked before and after sampling.

The type of filter used depends on the contaminant to be measured. Charcoal filters are used for radioiodines, whereas glass fibre or paper filters are used for gross beta/gamma particulate and water bubblers for tritiated water/vapour.

3.4.4 In-situ gamma spectrometers

In-situ gamma spectrometry is a rapid method for the assessment of gamma emitting ground surface contamination. In-situ gamma spectrometry measurements are subject to uncertainties due to many reasons, especially the deviation of the actual source distribution from the distribution assumed for the determination of the calibration factors applied. Allowance must be made to the nature of the site (open, smooth, plane areas, distant from disturbing objects would be ideal, where no agricultural or other activity is destroying the vertical concentration profile since the radionuclide deposition occurred). Care must be taken to place the detector in the defined position (1 metre above the ground with the detector head looking downwards).

In an emergency situation the conversion of the spectrum line intensities to surface contamination is usually done by assuming the radionuclides are distributed evenly on the plane of the ground surface. Depending on several conditions (dry or wet deposition, time elapsed since the accident, physico-chemical properties of the soil, surface roughness, etc.) this assumption may lead to an underestimation of the total activity of the contaminants initially deposited on a unit area of the ground. This deviation, however, is unlikely to exceed a factor of 2 if the measurement is done in the early or intermediate post-accident phase (that is, shortly after the deposition).

Due to the high sensitivity of both *NaI(Tl)* and *Ge* detectors the application of in-situ gamma spectrometry will get more and more difficult with increasing contamination levels. Dead time problems, spectrum peak shape distortions may seriously affect the results of the analyses. A standard *Ge* detector of 20 - 30 % of relative efficiency starts to deviate from its normal operation if the surface contamination exceeds *1 MBq/*m^2 for ^{137}Cs. Reduction of the detector sensitivity by shielding it or selecting other detectors of lower efficiency can extend the range of applicability by orders of magnitude.

Choosing the detector type depends on several circumstances and conditions. If available, *Ge* detectors have the advantage of high resolution, which permits more specific identification of individual radionuclides and as a consequence a more accurate determination of the activity of each radionuclide present in the sample. Its delicate design, sensitivity for damage and the need for cooling to very low temperatures more usually with liquid nitrogen, however, will limit the range of applicability. On the other hand the simpler, robust and durable *NaI(Tl)* scintillation detector has the advantage of withstanding the erosive effects of the environment but the user must be content with a limited resolution achievable with this type of detector. The selection of the detector also depends on the type of accident. For example environmental contamination of a single or few gamma emitters, such as ^{131}I or ^{137}Cs, can easily be assessed by *NaI(Tl)* whereas a mixture of many components will require high resolution *Ge* spectrometry.

3.4.5 Personal dosimeters

Personal dosimeters are needed for emergency personnel if required to enter high dose rate areas. The type of personal dosimeter available will depend on the local dosimetry service and may be a thermoluminescent dosimeter (TLD) badge, TLD bulb dosimeter, a film badge or a glass phosphate dosimeter. These types of dosimeters yield results that are historic in nature in that they need to be returned to a dosimetry service for processing and dose assessment. In emergency situations it is often desirable to have direct reading dosimeters to supplement these. The advantage in the latter is that the wearer can tell at the time what dose he/she has received to date or for a particular operation. Quartz fibre electrometers (QFE) are common direct reading instruments that are relatively inexpensive. Electronic direct reading personal dosimeters, also generally available, have the advantage that, in addition to giving a visual read out they can make an audible beep for each increment of dose received and be set to alarm at a predetermined level. An increase in audible beep rate immediately alerts the wearer to a change in the ambient dose rate in his or her vicinity. If direct reading dosimeters are not available to emergency monitoring teams, measurements made using dose rate meters may be used to estimate exposure of teams based on the time they remain at a particular location in a particular dose rate. Some types of dose rate meters also have an integrating dose capability.

3.5 Pathways of exposure

Radionuclides discharge into the environment can result in radiation exposure of people through a variety of mechanisms. Radioactive materials present in air, water or food can be inhaled or ingested into the body. Some of these materials may become incorporated in tissues or organs, thereby resulting in internal irradiation of body organs. The effect on people is normally expressed in terms of doses.

3.5.1 Dose Definition

Different kinds of radiation are accompanied by the release of a different quantity of energy and have a different penetrating ability. Therefore they cause different effects to live organisms.

Damages, which produce radiation in the organs or tissues, directly depend on amount of energy which is transferred to tissues or organs during interaction. The quantity of such energy, which will be transferred to an organism, is named a “*dose*”. A radiation dose can be transferred to an organism by any radionuclide or some mix of them independently from it position in space (out of body or inside body). Doses can be calculated in different ways. They can depend on the organ of the body, duration of exposure, or on the exposed person’s individual characteristics.

Absorbed dose of radiation is the amount of energy imparted by radiation to a unit mass of absorbing material. *Gray* (*Gy*) is the main absorbed dose unit in the *SI* system (*1Gy = 1J/1kg*). Sometimes one can use unit called a *Rad* (*1rad = 0.01 Gy*)

The absorbed dose is an integral quantity, corresponding to the energy deposition over time. Therefore sometimes one can use the term of *"absorbed dose rate"*.

Absorbed dose rate is the amount of energy imparted by radiation to a unit mass of absorbing material per unit time. Gray per second (*Gy/sec*) is the main absorbed dose rate unit in the *SI* system.

It should be mentioned that the value of an absorbed dose of radiation takes into account only the amount of imparted energy. Therefore for the same absorbed dose of radiation, the harmfulness of that dose will depend on the type of radiation and on the irradiated organ.

Quality factor Q is the weights of the absorbed dose according to the biological effectiveness of the radiation types producing the dose.

The quality factor does not depend on the organs or tissues which are under irradiation. The quality factor *Q* is defined as a function of the collision stopping power in water. For collision stopping power less than 3.5 *keV/μm* the quality factor is approximately equal to *1* (that value is used for X-ray, gamma rays and electrons). For collision stopping power equal to 7 *keV/μm*, the quality factor is approximately equal to *10* (that value is used for neutrons, protons and singly-charged particles of rest mass greater than one atomic mass unit of unknown energy). For collision stopping power greater than 175 *keV/μm*, the quality factor is approximately equal to *20* (that value is used for alpha particles, multiply charged particles of unknown energy).

Dose equivalent is the absorbed dose multiplied by the quality factor and multiplied by the product of other modifying factors. *Sievert* (*Sv*) is the main dose equivalent unit in the *SI* system (*1Sv = 1Gy x Q x product of other modifying factors*). Sometimes one can use a unit called a *Rem* (*1 Rem = 0.01 Sv*).

The value of other modifying factors for the product assigned by the ICRP is equal to one. The dose equivalent depends on type of radiation, but does not depend on the organ. The term of dose equivalent rate can be defined in the same way as in the definition for the absorbed dose rate.

To solve the problem of independence of dose equivalent from organ, the effective dose equivalent should be defined.

Effective dose equivalent is defined as the sum of dose equivalents to individual organs with each term weighted by organ weighted factor. For the effective dose equivalent the same unit is in use.

All the terms defined above describe only individual doses. Therefore, in international practice the term of *collective effective dose equivalent* is in use. This is just the simple sum of effective dose equivalents for such a group of people. The unit for a collective effective dose equivalent is man-sievert (*man-Sv*).

3.5.2 Exposure pathways

There is large number of different pathways of human exposure. But there are six principal pathways by which people can accumulate a radiation dose after an accident with radioactive materials:

- External irradiation from radioactive materials in the passing plume or cloud, referred to as "cloud shine"
- External irradiation from radioactive materials deposited on the ground, referred to as "ground shine"
- External irradiation from radioactive materials deposited on the skin and clothing
- Internal irradiation from radioactive materials inhaled from the passing plume

- Internal irradiation from radioactive materials inhaled following re-suspension of the ground deposit
- Internal irradiation from radioactive materials ingested following the contamination of foodstuffs

During normal operation of radioactive materials for peaceful purposes, people can externally or internally be exposed. The hazard of main radioisotopes is detailed in Table 25.

Table 25 **Radioisotopes, type of radiation and target organs**

Radioisotope	Type of radiation	Hazard	Target organ
H-3	Beta	Internal	Whole body
C-14	Beta	Internal	Whole body
P-32	Beta	Internal	Whole body
N-16	Beta, Gamma	External	Whole body
Kr-85	Beta, Gamma	External	Whole body
Co-60	Beta, Gamma	External / internal	Whole body
Sr-90	Beta	Internal	Bone surfaces
I-131	Beta, Gamma	External / internal	Thyroid
Xe-133	Beta, Gamma	External	Whole body
Tc-99	Beta	Internal	Stomach wall
Cs-137	Beta, Gamma	External / internal	Whole body
Ir-192	Beta, Gamma	External / internal	Whole body
Rn-222 + progeny	Alpha, Beta, Gamma	External / internal	Bronchial epithelium of lung
U-238	Alpha	Internal	Bone surfaces
Th-232	Alpha	Internal	Bone surfaces
Pu-238	Alpha	Internal	Bone surfaces

External irradiation

Both beta and gamma emitters in the air contribute to individual external exposures. Because of its short average travelling distance in the air (a few meters) and limited penetration (skin irradiation only), the contribution to the dose from beta particles is often neglected. Therefore, the dose of external exposure due to this pathway is mainly depend on gamma radiation. The dose greatly depends on time because of deposition processes.

As in the case of airborne radionuclides, the contribution from beta particles to an external dose from deposited radionuclides is generally neglected. The magnitude of the gamma dose received by an individual from deposited radionuclides depends not only on the length of time for which the individual is exposed, but also on the behaviour at the time of the deposited radionuclides. Radioactive decay will result in reduction of the dose rate with time. Additionally, natural weathering processes may remove the deposit from the exposed surface.

Both beta and gamma emitters contribute to individual external exposure following deposition of radioactive material onto the skin and clothing. The dose received is generally evaluated by multiplying the amount of radioactive material deposited on the skin and clothing by pre-calculated dose per unit activity of particular radionuclide.

Internal irradiation

The evaluation of potential exposures to radioactive materials presents rather complex problems, which must be considered for each radionuclide in various chemical forms of particulate dispersion. Each chemical form of each element has different specific properties of solubility, transfer across membranes, distribution among the various tissues in the body, in some cases deposition in certain tissues and finally excretion from the body.

The principal factors considered in an internal exposure evaluation include:

- the chemical form in which the various nuclides occur
- the relative abundance of the nuclides,
- the characteristics of the aerosol or the fine powder in which the nuclides occur
- the aerodynamic behaviour of the aerosol particles as they are inhaled and deposited in various sections of the respiratory system,
- the movement of particles within the respiratory tract and out of it into the lymphatic system and the gastrointestinal tract
- the absorption of the nuclide into the bloodstream
- the distribution of the radionuclide among organ and tissues
- the retention of the nuclide by the body.

In addition, each radionuclide emits different types of radiation.

3.6 Health consequences

Ionising radiation is believed to interact with the human body by two different mechanisms: the indirect effect and the direct effect. The first effect refers to radiation interaction with body water, whereas the direct effect refers to direct interaction with critical biological molecules.

3.6.1 Indirect effect

Water is basic to all living tissues. Actually, 80% of all soft tissues in the human body are water. In the theory of the indirect effect, or radiolysis of water, radiation interacts with body water to produce toxic free radicals (free radical is a chemical species with an unpaired electron; it does not carry an electrical charge). These toxic free radicals are powerful oxidizing agents, which migrate to and attack biological molecules, hence the term indirect effect. One of the most important of these is the hydroxyl, or OH radical. Two of these hydroxyl radicals combine as follows:

$OH + OH = H_2O_2$ (hydrogen peroxide)

Hydrogen peroxide can attack and damage biological molecules by breaking chemical bonds. Since cells are made up mainly of water, it is believed that this indirect mechanism of cell damage is more likely occur than the direct effect.

3.6.2 Direct Effect

In the theory of the direct effect, radiation directly interacts with critical biological molecules in the human cell.

Of all the structures of the human cell, the DNA in the cell nucleus is believed to be the most sensitive to radiation and therefore the critical biological target for radiation damage. Radiation breaks chemical bonds in the DNA on the chromosomes in the cell nucleus, thereby causing mutations. Since the DNA directs both cell function and inherited information passed along in cell division and reproduction, any changes to the DNA can result in radiation damage being expressed in the organism itself. Both cell death (includes the inability to divide or reproduce) and cell mutation are involved. Typical normal chromosomes are in X form. Radiation-induced chromosome aberrations (damage) are terminal deletion, reparation in ring structure and reparation in dysenteric structure.

3.6.3 High dose effects (acute radiation syndrome)

For the purposes of this discussion, high dose effects are those resulting from a whole body dose above 1 *Gy* delivered acutely, that is, over a period of a few seconds to a few hours. These effects include the acute radiation syndrome, skin damage, cataracts, and sterility.

The above types of effects are also called “non-stochastic” effects. A non-stochastic effect is one, which has a well-defined threshold, which must be exceeded for the effect to occur; and where the severity of the effect varies with the radiation dose. Non-stochastic effects can be avoided altogether if dose limits are set below the threshold for the effects.

3.6.4 Acute radiation syndrome

The acute radiation syndrome is divided into three levels of effects:

- the haematopoietic or blood syndrome
- the gastrointestinal or *GI* syndrome
- the central nervous system or *CNS* syndrome

The dose threshold for the haematopoietic syndrome is about 1 *Gy* for whole body exposure. Below about 1 *Gy* there would be no overt clinical symptoms of radiation exposure. Chromosome aberrations could be detected in a sample of blood from individuals exposed to as little as about 0.2 *Gy* acute dose, but there would be no apparent symptoms detected clinically. The organ at risk in the blood system syndrome is the bone marrow. Death is possible within 2-8 weeks at doses over 2 *Gy*. Death results from infection, bleeding and anaemia.

The next syndrome is the *GI* syndrome, with a threshold of about 5 *Gy*. The organ at risk is the intestinal lining. Effects include nausea, vomiting, and diarrhoea (in addition to those effects from the blood system syndrome). Death is likely within 3-14 days at doses over 10 *Gy*. Causes of death include infection, bleeding, dehydration, electrolyte imbalance, and circulatory collapse.

A concept used in connection with the acute radiation syndrome is called the LD50/30 (sometimes written as LD50/60), which is the dose at which 50% of the exposed individuals will die within 30 (or 60) days without medical treatment. The LD50/30 for human beings is about 4 *Gy* acute whole body dose. Since no two individuals respond in exactly the same way to radiation exposure, statistical concepts such as the LD50/30 have been devised to describe the response of a population of individuals to radiation exposure. Medical treatment is generally effective for doses below about 10 *Gy*. Acute exposures above about 10 *Gy* are usually fatal.

The third and final acute radiation syndrome is the CNS syndrome, with a threshold of about 20 *Gy*. The organ at risk is the brain. It appears that the principal effect is the brain's inability to control muscles such as the heart. Effects include lethargy, convulsions, tremors, loss of muscle control, and coma (in addition to all the effects seen for the blood and *GI* syndromes). Death is likely within 3 days for doses over 50 *Gy*. Causes of death include respiratory and circulatory collapse.

3.6.5 Low dose effects

The principal effect of low doses of radiation (that is, below about 0.1 *Gy*) is non-lethal cell mutations, with the greatest concern being cancer induction. The effects can take years to manifest themselves, so they are often called *"late effects"* of radiation exposure.

Low dose effects are also called *"stochastic"* effects. Stochastic effects are health effects that occur randomly, and the probability of the effect rather than the severity is assumed to be linear and without a threshold. Cancer and hereditary effects are examples of stochastic effects.

There are three general categories of effects resulting from exposure to low doses of radiation: somatic, genetic, and in utero.

Somatic effects are those suffered by the individual exposed. Cancer is the principal example of a somatic effect. Radiation cancer has definitely been linked to acute radiation doses above about 0.25 - 0.35 *Gy*, for example, in survivors of the Hiroshima and Nagasaki atomic bombings. Other populations where such a link has been established include uranium miners (lung cancer), radium dial painters (bone cancer), patients who have received large doses of therapeutic radiation, and radiologists (skin cancer).

Principal radiation-induced cancers include leukaemia and the solid tumours such as thyroid, lung, breast, and bone cancers.

Leukaemia has been observed to have a latency period of only 2 to 3 years, whereas the solid tumours have latency periods of 10 to 20 years or more.

Radiation-induced cancer has never been proven at occupational doses and below (5 *Rem/yr* or less).

Genetic effects of radiation are those that are passed to the offspring of the individuals exposed. The effect involves mutation of sperm and egg cells. Radiation-induced genetic effects have been definitely observed in experiments with mice and fruit flies, but have never been definitively proven to occur in human beings at any dose level. Radiation does *not* produce any new mutations but simply increases the spontaneous mutation rate, with the effect appearing to be proportional to dose with no threshold.

Some possible explanations (speculations) for why radiation-induced genetic effects have never been observed in human beings is that:

- the mutations in the reproductive cells produce such significant changes in the fertilized egg that the result is a non-viable organism which is spontaneously aborted during the earliest stages and is never detected
- radiation-induced genetic effects are recessive in nature and would take several generations to manifest themselves, consequently we have not had enough time to follow them to their complete expression in the descendants of exposed individuals

Genetic risks from 1 *Rem* of radiation exposure to the reproductive organs are approximately 50-1,000 times less than the spontaneous risk for various anomalies.

3.6.6 In utero exposure

Radiation is capable of producing physical malformations during foetal development. These effects can be considered a subset of the general category of somatic effects. The principal effects of exposure in utero are intrauterine death, growth retardation, mental retardation (maximum risk believed to be between 8 to 15 weeks gestation), developmental abnormalities, and childhood cancer.

Since organ systems in the embryo/foetus develop during the first three months of pregnancy, radiation exposure during this period (first trimester) is considered to pose the greatest risk. The risk of all in utero effects is about 1-10 per 1,000 rem. Normal risks of foetal abnormalities are about 5-30 per 1,000 live births.

3.7 Radiation protection

3.7.1 Basic principles of radiation protection

The principles of radiation protection and safety are presented in the *International Basic Safety for Protection against Ionising Radiation* or in appropriate national regulations (Standards).

A summary of the principles is as follows:

- practice that entails or that could entail exposure to radiation should only be adopted if it yields sufficient benefit to the exposed individuals or to society to outweigh the radiation detriment it causes or could cause (that is, the practice must be justified)
- individual doses due to the combination of exposures from all relevant practices should not exceed specified dose limits
- radiation sources and installations should be provided with the best available protection and safety measures under the prevailing circumstances, so that the magnitudes and likelihood of exposures and the numbers of individuals exposed be as low as reasonably achievable, economic and social factors being taken into account, and the doses they deliver and the risk they entail be constrained (that is, protection and safety should be optimised)
- radiation exposure due to sources of radiation that are not part of a practice should be reduced by intervention when this is justified, and the intervention measures should be optimised; the person legally authorized to engage in a practice involving a source of radiation should bear the primary responsibility for protection and safety
- a safety culture should be inculcated that governs attitudes and behaviour in relation to protection and safety of all individuals and organisations dealing with sources of radiation; in-depth defensive measures should be incorporated into the design and operating procedures for radiation sources to compensate for potential failures in protection or safety measures
- protection and safety should be ensured by sound management and good engineering, quality assurance, training and qualification of personnel, comprehensive safety assessments and attention to lessons learned from experience and research

3.7.2 Legal aspects

Registrants and licensees and employers of workers who are engaged in activities involving normal exposures or potential exposure shall be responsible for:

- the protection of workers from occupational exposure
- compliance with any other relevant requirements of the Standards

Employers, registrants and licensees shall ensure, for all workers engaged in activities that involve or could involve occupational exposure, that:

- occupational exposures be limited as specified in Standards
- occupational protection and safety be optimised in accordance with the relevant principal requirements of the Standards
- decisions regarding measures for occupational protection and safety be recorded and made available to the relevant parties, through their representatives where appropriate, as specified by the Regulatory Authority
- policies, procedures and organisational arrangements for protection and safety be established for implementing the relevant requirements of the Standards, with priority given to design and technical measures for controlling occupational exposures
- suitable and adequate facilities, equipment and services for protection and safety be provided, the nature and extent of which are commensurate with the expected magnitude and likelihood of the occupational exposure
- necessary health surveillance and health services be provided
- appropriate protective devices and monitoring equipment be provided and arrangements made for its proper use
- suitable and adequate human resources and appropriate training in protection and safety be provided, as well as periodic retraining and updating as required in order to ensure the necessary level of competence
- adequate records be maintained as required by the Standards
- arrangements be made to facilitate consultation and co-operation with workers with respect to protection and safety, through their representatives where appropriate, about all measures necessary to achieve the effective implementation of the Standards
- necessary conditions to promote a safety culture be provided

Registrants or licensees shall, as a precondition for engagement of workers who are not their employees, obtain from the employers, including self-employed individuals, the previous occupational exposure history of such workers and other information as may be necessary to provide protection and safety in compliance with the Standards.

If workers are to be engaged in work that involves or could involve a source that is not under the control of their employer, the registrant or licensee responsible for the source shall provide:

- appropriate information to the employer for the purpose of demonstrating that the workers are provided with protection in accordance with the Standards
- such additional available information about compliance with the Standards as the employer may request prior to, during and after the engagement of such workers by the registrant or licensee

Employers, registrants and licensees shall take such administrative actions as are necessary to ensure that workers are informed that protection and safety are integral parts of a general occupational health and safety programme in which they have certain obligations and responsibilities for their own protection and the protection of others against radiation and for the safety of sources.

Employers, registrants and licensees shall facilitate compliance by workers with the requirements of the Standards.

Workers shall:

- follow any applicable rules and procedures for protection and safety specified by the employer, registrant or licensee
- use properly the monitoring devices and the protective equipment and clothing provided
- co-operate with the employer, registrant or licensee with respect to protection and safety and the operation of radiological health surveillance and dose assessment programmes
- provide to the employer, registrant or licensee such information on their past and current work as is relevant to ensure effective and comprehensive protection and safety for themselves and others
- abstain from any willful action that could put themselves or others in situations that contravene the requirements of the Standards
- accept such information, instruction and training concerning protection and safety as will enable them to conduct their work in accordance with the requirements of the Standards

If for any reason a worker is able to identify circumstances that could adversely affect compliance with the Standards, the worker shall as soon as feasible report such circumstances to the employer, registrant or licensee.

Employers, registrants or licensees shall record any report received from a worker that identifies circumstances which could affect compliance with the Standards, and shall take appropriate action.

Registrants and licensees shall, as a precondition for engagement of workers in activities that involve or could involve exposure from a source not under the registrant's or licensee's control, provide the employer with any information about worker protection under the Standards which the employer requests in order for the employer to demonstrate compliance with other applicable laws and regulations governing workplace hazards.

No worker undertaking an intervention shall be exposed in excess of the maximum single year dose limit for occupational exposure, except:

- for the purpose of saving life or preventing serious injury
- if undertaking actions intended to avert a large collective dose
- if undertaking actions to prevent the development of catastrophic conditions

When undertaking intervention under these circumstances, all reasonable efforts shall be made to keep doses to workers below *twice the maximum single year dose limit* (*10 mSv*), except for life saving actions, in which every effort shall be made to keep doses below *ten times the maximum single year dose limit* in order to avoid deterministic effects on health (50 mSv). In addition, workers undertaking actions in which their doses may approach or exceed ten times the maximum single year dose limit shall do so only when the benefits to others clearly outweigh their own risk.

Workers who undertake actions in which the dose may exceed the maximum single *year dose limit shall be volunteers* and shall be clearly and comprehensively informed in advance of the associated health risk, and shall, to the extent feasible, be trained in the actions that may be required.

The legal person responsible for ensuring compliance with the foregoing requirements shall be specified in emergency plans.

All reasonable steps shall be taken to provide appropriate protection during the emergency intervention and to assess and record the doses received by workers involved in emergency intervention. When the intervention has ended, the doses received and the consequent health risk shall be communicated to the workers involved.

Workers shall not normally be precluded from incurring further occupational exposure because of doses received in an emergency exposure situation. However, qualified medical advice shall be obtained before any such further exposure if a worker who has undergone an emergency exposure receives a dose exceeding ten times the maximum single year dose limit or at the worker’s request.

Annex 1: Glossary

The terms set out below are defined for the purposes of this module, only. To the extent possible, common definitions of these terms are used.

Acceptability/tolerability of risk: A willingness to live with a risk, in order to secure certain benefits.

Accident: Any unplanned, sudden event which causes or is liable to cause injury to people or damage to buildings, plant, material or the environment.

Affiliates: Enterprises in which another enterprise has minority voting rights without effective operational control.

(**Safety) Audit:** A methodical in-depth examination of all or part of a total operating system with relevance to safety.

Chemical industry: Enterprises which produce, formulate and/or sell chemical substances, including petrochemicals.

Contractors: Includes all contractors and subcontractors.

Consequence: Result of a specific event.

Emergency Preparedness Plan (or) Emergency Plan: A formal written plan which, on the basis of identified potential accidents together with their consequences, describes how such accidents and their consequences should be handled either on-site or off-site.

Employee: A person who is under a contract of employment with an enterprise, including management.

Enterprise: A company or corporation (including transnational corporations) which has operations involving the production, processing, handling, storage, use or disposal of hazardous substances.

Ergonomics: A discipline concerned with designing plant, equipment, operation and work environments so that they match human capabilities.

Event: The realisation of a hazard.

Event tree analysis: One of several methods of hazard analysis involving inductive determination of pathways of disturbances having led to a hazardous situation.

Fault tree analysis: One of several methods of hazard analysis, involving deductive description of events leading from failures of components to a hazardous situation.

Hazard: An inherent property of a substance, agent, source of energy or situation having the potential of causing undesirable consequences.

Hazard analysis: Identification of individual hazards of a system, determination of the mechanisms by which they could give rise to undesired events, and evaluation of the consequences of these events.

Hazardous installation: A fixed industrial plant/site at which hazardous substances are produced, processed, handled, stored, used or disposed of in such a form and quantity that there is a risk of a major accident involving hazardous substance (s) which could cause serious harm to human health or damage to the environment, including property.

Hazard and Operability Study (HAZOP): One of several methods of hazard analysis carried out by application of guide words to engineering and instrument drawings to identify all deviations from design intent with undesirable effects for safety or Operability, with the aim of identifying potential hazards.

Hazardous substance: An element, compound, mixture or preparation which, by virtue of its chemical, physical or (eco) lexicological properties, constitutes a hazard.

Incidents: Accidents and/or near-misses.

Information: Facts or data or other knowledge which can be provided by any means including, for example, electronic, print, audio or visual.

Land-use planning: Consists of various procedures to achieve both general zoning/physical planning as well as case-by-case decision-making concerning the siting of an installation or of other developments.

Major Accident: Any unplanned, sudden event which causes or is liable to cause serious injury to people or damage to buildings, plant, material or the environment.

Management: Employees at, or owners of, a hazardous installation who have the responsibility and authority to take decisions concerning the operation of an installation, including decisions relevant to safety and, where appropriate, employees at a corporate level in the enterprise having such authority.

Monitor (or) monitoring: Use of checks, inspections, tours, visits, sampling and measurements, surveys, reviews or audits to measure compliance with relevant laws, regulations, standards, codes, procedures and/or practices; includes activities of public authorities, industry and independent bodies.

Near-miss: Any unplanned, sudden event which, but for the mitigation effects of safety systems or procedures, could have caused serious injury to people or serious damage to buildings, plant, material or the environment or could have involved a loss of containment possibly giving rise to significant adverse effects.

Notification: A requirement to provide specified information related to a hazardous installation in an appropriate manner to competent authorities.

OECD-based enterprise: Enterprise whose corporate headquarters or effective operational control is located in an OECD Member country.

Probability: The likelihood that a considered occurrence will take place.

Product stewardship: A system of managing products through all stages of their life cycle including customer use and disposal (with the objective of continuously improving safety for health and the environment).

Public authorities: Government bodies at national, regional, local and international level with the authority to issue licenses, regulations, standards or other instructions having the force of law.

Reasonably practicable: All which is possible subject to the qualification that the costs of the measures involved are not grossly disproportionate to the value of the benefits obtained from these measures.

Residual risk: The risk still remaining after the implementation of risk management practices.

Risk: The combination of a consequence and the probability of its occurrence.

Risk assessment: The value judgment of the significance of the risk, identified by a risk analysis taking into account any relevant criteria.

Risk management: Actions taken to achieve or improve the safety of an installation and its operation.

Safety: A situation without unacceptable risks. For purposes of this text, “safety” embraces health, safety and environmental protection, including protection of property.

Safety report: The written presentation of the technical, management and operational information concerning the hazards of a hazardous installation and their control in support of a justification for the safety of the installation.

Storage facilities: Warehouses, lank farms and other facilities where hazardous substances are held.

Subsidiaries: Enterprises in which another enterprise has majority voting rights and/or effective operational control.

Transfer of technology: The movement of process and other safety-related technology from one country to another, embracing not only the actual transfer but also the application of the technology as well as the operation of the plant.

Trans-frontier damage: Any serious damage to human health or the environment, including property, in the event of an accident suffered by a country other than the country where the accident originated.

Warehousekeeper: The person responsible for a storage facility, whether on the site of a hazardous installation or off-site.

Annex 2: Definitions

The definitions set out below are pertinent to this module, only. To the extent possible, they are in common definitions used in other modules.

Hazardous installation: an industrial installation which contains more than the threshold quantity of any of the hazardous substances mentioned in Annex 3 and in which are used, stored or produced such hazardous substances which are capable, in the event of an accident, of causing serious damage to human health or the environment, including property, outside the installation site, with the exclusion of military or nuclear installations

Proposal for a hazardous installation: any proposal made to a competent authority to set up a new hazardous installation and any proposal involving substantial modification of an existing hazardous installation

Accident: any occurrence involving a hazardous substance such as a major emission, fire or explosion at a hazardous installation leading to serious damage to human health or the environment, including property

Hazardous substance: any substance which is capable of causing serious damage to human health or the environment, including property, in the event of an accident in a hazardous installation and which is identified in Annex 3

Trans-frontier damage: any serious damage to human health or the environment, including property, suffered by an exposed country in the event of an accident and, in general, by the country of the accident

Sensitive group: any group of persons particularly sensitive to the consequences of an accident as a result of their age, health conditions or way of life

Country of the installation: any country within whose jurisdiction there is a hazardous installation or a proposal for a hazardous installation

Exposed country: any country other than the country of the installation which suffers serious damage as a result of an accident, or which is capable of being affected by such damage in an area under its national jurisdiction

Countries concerned: the country of the installation in the exposed country or countries

Annex 3: Threshold quantities of hazardous substances

Flammable, explosive or oxidizing substances		Substances toxic to man and/or the environment	
Hazardous substance	**Threshold (tonnes)**	**Hazardous substance**	**Threshold (tonnes)**
Flammable gases* including liquefied flammable gases	200	Ammonia	500
		Chlorine	25
		Hydrogen cyanide	20
Highly flammable liquids**	50,000	Hydrogen fluoride	50
Ethylene oxide	50	Methyl isocyanate	0.15
Sodium chlorate	250	Sulphur dioxide	250
Ammonium nitrate	2,500	Acrylonitrile	200
		Hydrogen sulphide	50
		Phosgene	0.75
		Methylbromide	200
		Tetraethyl lead	50
		Disulfoton	0.1
		Parathion	0.1
		Warfarin	0.1
		Aldicarb	0.1

(*) - *Flammable gases:* Substances which in the gaseous slate at normal pressure and mixed with air become flammable and the boiling point of which at normal pressure is 20<1°C or below.

(**) - *Highly flammable liquids:* Substances which have a flash point lower than 21°C and the boiling point of which at normal pressure is above 20°C.

The hazardous substances and threshold quantities mentioned above are without prejudice to those used in more extensive lists of hazardous installations developed in a national or international context.

Annex 4: Safety phrases concerning dangerous chemical substances and preparations used in EU Countries

Label	Preparation
S1	Keep locked up
S2	Keep out of the reach of children
S3	Keep in a cool place
S4	Keep away from living quarters
S5	Keep contents under ... [appropriate liquid to be specified by the manufacturer]
S6	Keep under ... [inert gas to be specified by the manufacturer]
S7	Keep container tightly closed
S8	Keep container dry
S9	Keep container in a well-ventilated place
S12	Do not keep container sealed
S13	Keep away from food, drink and animal feeding stuffs
S14	Keep away from ... [incompatible materials to be indicated by the manufacturer]
S15	Keep away from heat
S16	Keep away from sources of ignition - No smoking
S17	Keep away from combustible material
S18	Handle and open container with care
S20	When using do not eat or drink
S21	When using do not smoke
S22	Do not breathe dust
S23	Do not breathe gas / fumes / vapour / spray [appropriate wording to be specified by the manufacturer]
S24	Avoid contact with skin
S25	Avoid contact with eyes
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S27	Take off immediately all contaminated clothing
S28	After contact with skin, wash immediately with plenty of ... [to be specified by the manufacturer]
S29	Do not empty into drains
S30	Never add water to this product
S33	Take precautionary measures against static discharges
(S34)	(Avoid shock and friction)
S35	This material and its container must be disposed of in a safe way
S36	Wear suitable protective clothing
S37	Wear suitable gloves
S38	In case of insufficient ventilation, wear suitable respiratory equipment
S39	Wear eye/face protection
S40	To clean the floor and all objects contaminated by this material, use ... [to be specified by the manufacturer]
S41	In case of fire and/or explosion, do not breathe fumes
S42	During fumigation/spraying, wear suitable respiratory equipment [appropriate wording to be specified by the manufacturer]
S43	In case of fire, use ... [indicate in the space the precise type of fire-fighting equipment. If water increases the risk, add - Never use water]
(S44)	If you feel unwell, seek medical advice [show the label where possible]
S45	In case of accident or if you feel unwell, seek medical advice immediately [show the label where possible].
S46	If swallowed, seek medical advice immediately and show this container or label.
S47	Keep at temperature not exceeding ...°C [to be specified by the manufacturer].
S48	Keep wetted with ... [appropriate material to be specified by the manufacturer]
S49	Keep only in the original container
S50	Do not mix with ... [to be specified by the manufacturer]

Label	Preparation
S51	Use only in well-ventilated areas
S52	Not recommended for interior use on large surface areas
S53	Avoid exposure - obtain special instructions before use
(S54)	(Obtain the consent of pollution control authorities before discharging to wastewater treatment plants)
(S55)	(Treat using the best available techniques before discharge into drains or the aquatic environment)
S56	Dispose of this material and its container at hazardous or special waste collection point
S57	Use appropriate container to avoid environmental contamination
(S58)	(To be disposed of as hazardous waste)
S59	Refer to manufacturer/supplier for information on recovery/recycling
S60	This material and its container must be disposed of as hazardous waste
S61	Avoid release to the environment. Refer to special instructions/Safety data sheets
S62	If swallowed do not induce vomiting: seek medical advice immediately and show this container or label
	Combination of S-Phrases
S1/2	Keep locked up and out of reach of children
S3/7	Keep container tightly closed in a cool place
(S3/9)	(Keep in a cool, well-ventilated place)
(S3/7/9)	(Keep container tightly closed in a cool, well-ventilated place)
S3/9/14	Keep in a cool, well-ventilated place away from ... [incompatible materials to be indicated by the manufacturer]
S3/9/49	Keep only in the original container in a cool, well-ventilated place
S3/9/14/49	Keep only in the original container in a cool, well-ventilated place away from ... [incompatible materials to be indicated by the manufacturer]
S3/14	Keep in a cool place away from ... [incompatible materials to be indicated by the manufacturer]
S7/8	Keep container tightly closed and dry
S7/9	Keep container tightly closed and in a well-ventilated place
S20/21	When using do not eat, drink or smoke
S24/25	Avoid contact with skin and eyes
S36/37	Wear suitable protective clothing and gloves
S36/39	Wear suitable protective clothing and eye/face protection
S37/39	Wear suitable gloves and eye/face protection
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection
S47/49	Keep only in the original container at temperature not exceeding...°C [to be specified by the manufacturer]
S3/7	Keep container tightly closed in a cool place
S7/47	Keep container tightly closed and at a temperature not exceeding...°C [to be specified by the manufacturer]
S29/56	Do not empty into drains, dispose of this material and its container at hazardous or special waste collection point

(Phrases in parenthesis) are no longer in use

Annex 5: Risk Phrases Used in EU Countries

Label	Nature of risks
R1	Explosive when dry
R2	Risk of explosion by shock, friction, fire or other sources of ignition.
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition
R4	Forms very sensitive explosive metallic compounds
R5	Heating may cause an explosion
R6	Explosive with or without contact with air
R7	May cause fire
R8	Contact with combustible material may cause fire
R9	Explosive when mixed with combustible material
R10	Flammable
R11	Highly flammable
R12	Extremely flammable
(R13)	(Extremely flammable liquified gas)
R14	Reacts violently with water
R15	Contact with water liberates highly flammable gases
R16	Explosive when mixed with oxidizing substances
R17	Spontaneously flammable in air
R18	In use, may form flammable/explosive vapour-air mixture
R19	May form explosive peroxides
R20	Harmful by inhalation
R21	Harmful in contact with skin
R22	Harmful if swallowed
R23	Toxic by inhalation
R24	Toxic in contact with skin
R25	Toxic if swallowed
R26	Very toxic by inhalation
R27	Very toxic in contact with skin
R28	Very toxic if swallowed
R29	Contact with water liberates toxic gases
R30	Can become highly flammable in use
R31	Contact with acids liberates toxic gas
R32	Contact with acids liberates very toxic gas
R33	Danger of cumulative effects
R34	Causes burns
R35	Causes severe burns
R36	Irritating to eyes
R37	Irritating to respiratory system
R38	Irritating to skin
R39	Danger of very serious irreversible effects
R40	Possible risks of irreversible effects
R41	Risk of serious damage to eyes
R42	May cause sensitisation by inhalation
R43	May cause sensitisation by skin contact
R44	Risk of explosion if heated under confinement
R45	May cause cancer
R46	May cause heritable genetic damage
(R47)	(May cause birth defects)
R48	Danger of serious damage to health by prolonged exposure
R49	May cause cancer by inhalation
R50	Very toxic to aquatic organisms
R51	Toxic to aquatic organisms
R52	Harmful to aquatic organisms
R53	May cause long-term adverse effects in the aquatic environment
R54	Toxic to flora
R55	Toxic to fauna
R56	Toxic to soil organisms
R57	Toxic to bees
R58	May cause long-term adverse effects in the environment
R59	Dangerous for the ozone layer
R60	May impair fertility
R61	May cause harm to the unborn child
R62	Possible risk of impaired fertility
R63	Possible risk of harm to the unborn child
R64	May cause harm to breastfed babies

	Combination of R-phrases
R14/15	Reacts violently with water liberating highly flammable gases
R15/29	Contact with water liberates toxic, highly flammable gas
R20/21	Harmful by inhalation and in contact with skin
R20/22	Harmful by inhalation and if swallowed
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed
R21/22	Harmful in contact with skin and if swallowed
R23/24	Toxic by inhalation and in contact with skin
R23/25	Toxic by inhalation and if swallowed
R23/24/25	Toxic by inhalation, in contact with skin and if swallowed
R24/25	Toxic in contact with skin and if swallowed

Label	Nature of risks
R26/27	Very toxic by inhalation and in contact with skin
R26/28	Very toxic by inhalation and if swallowed
R26/27/28	Very toxic by inhalation, in contact with skin and if swallowed
R27/28	Very toxic in contact with skin and if swallowed
R36/37	Irritating to eyes and respiratory system
R36/38	Irritating to eyes and skin
R36/37/38	Irritating to eyes, respiratory system and skin
R37/38	Irritating to respiratory system and skin
R39/23	Toxic: danger of very serious irreversible effects through inhalation
R39/24	Toxic: danger of very serious irreversible effects in contact with skin
R39/25	Toxic: danger of very serious irreversible effects if swallowed
R39/23/24	Toxic: danger of very serious irreversible effects through inhalation and in contact with skin
R39/23/25	Toxic: danger of very serious irreversible effects through inhalation and if swallowed
R39/24/25	Toxic: danger of very serious irreversible effects in contact with skin and if swallowed
R39/23/24/25	Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed
R39/26	Very toxic: danger of very serious irreversible effects through inhalation
R39/27	Very toxic: danger of very serious irreversible effects in contact with skin
R39/28	Very toxic: danger of very serious irreversible effects if swallowed
R39/26/27	Very toxic: danger of very serious irreversible effects through inhalation and in contact with skin
R39/26/28	Very toxic: danger of very serious irreversible effects through inhalation and if swallowed
R39/27/28	Very toxic: danger of very serious irreversible effects in contact with skin and if swallowed
R39/26/27/28	Very toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed
R40/20	Harmful: possible risk of irreversible effects through inhalation
R40/21	Harmful: possible risk of irreversible effects in contact with skin
R40/22	Harmful: possible risk of irreversible effects if swallowed
R40/20/21	Harmful: possible risk of irreversible effects through inhalation and in contact with skin
R40/20/22	Harmful: possible risk of irreversible effects through inhalation and if swallowed
R40/21/22	Harmful: possible risk of irreversible effects in contact with skin and if swallowed
R40/20/21/22	Harmful: possible risk of irreversible effects through inhalation, in contact with skin and if swallowed
R42/43	May cause sensitisation by inhalation and skin contact
R48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation
R48/21	Harmful: danger of serious damage to health by prolonged exposure in contact with skin
R48/22	Harmful: danger of serious damage to health by prolonged exposure if swallowed
R48/20/21	Harmful: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin
R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R48/21/22	Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed
R48/20/21/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation
R48/24	Toxic: danger of serious damage to health by prolonged exposure in contact with skin
R48/25	Toxic: danger of serious damage to health by prolonged exposure if swallowed
R48/23/24	Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin
R48/23/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R48/24/25	Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed
R48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment

(Phrases in parenthesis) are no longer in use

Design: J&D graphics