

Chemical Waste Management for Laboratories

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Introduction

Ever since humans have inhabited the earth, they have been confronted with the problem of what to do with their waste materials.

Waste materials are substances which are no longer of use. Waste is defined by Wikipedia as an “unwanted or unusable material” or “substance which is discarded after primary use, or it is worthless, defective and of no use”. They may be in the form of solids, liquids or gases in a container. Waste materials may also include hazardous residues.

The adequate disposal of residual chemicals is an important factor in nature preservation, specifically the protection of air and water, soil and forests and the preservation of quality of life.

Whilst the disposal of waste is generally regulated by relevant laws, the first priority should always be the prevention of waste. Where prevention is considered not possible, the order of treatment should be reuse, recycling and, finally, other recovery and disposal methods. The environmentally compatible avoidance and utilization of the waste is always of uppermost importance.

In developing countries, however, there are often no specific rules for waste management or instructions about its treatment or elimination. Suitable disposal facilities, such as high temperature waste incineration plants or controlled landfills for hazardous waste are often lacking, with the result that chemical residues are often simply poured into the sink or treated as domestic waste, without considering the possible damage to nature, the environment and human health.

This manual is primarily intended to help responsible parties identify the most practical and application-oriented solutions for the disposal of chemical waste in developing countries. On the basis of general and specific procedures and examples, it demonstrates the possibilities available to a chemist or person in charge of a chemical laboratory regarding the selection of chemicals and their pre-treatment to ensure that no hazardous substances will be freed into the environment.

Waste from laboratories and research facilities is divided into special categories, some of which require particular attention and disposal. Waste legislation divides waste into non-hazardous and hazardous categories.

Non-hazardous waste:

Communal Waste

All solid waste with the exception of infectious, chemical or radioactive waste is considered communal waste. This waste stream can include items such as packaging materials and office supplies. Generally, it can be disposed of in a communal landfill or other such arrangements. Separating materials that can be reused or recycled greatly reduces the impact burden of this waste stream.

Hazardous waste:

Infectious

Infectious waste constitutes discarded material from medical or veterinary activities which have the potential of transmitting infectious agents to humans as well as discarded objects or equipment from the diagnosis, treatment and prevention of disease (such as assessment of health status or identification purposes) that have been in contact with blood and its derivatives (tissues, tissue fluids or excreta) or wastes from quarantine wards. Sharp items such as syringe needles, scalpels, infusion sets, knives, blades, broken glass, etc., whether contaminated or not, should be considered as a subgroup of infectious healthcare waste.

Pharmaceutical

This type of waste is made up of pharmaceuticals or materials containing pharmaceuticals (including expired medications) and items containing or contaminated with pharmaceuticals (bottles, boxes, containers and packaging).

Biological and microbiological

These types of hazardous waste contain substances with infectious properties from laboratories, including contaminated bottles and equipment.

Chemical

Chemical waste consists of or contains chemical substances, including laboratory chemicals, film developer, disinfectants (expired or no longer in use), solvents, cleaning agents and others types.

Radioactive

This waste includes unused liquids from radiotherapy or laboratory research, contaminated glassware or packages.

Legislative framework

Every country should have a legislative framework for chemical waste management. Not only suitable laws and regulations are important, but also methods for their enforcement and control must be stated.

Issues to be considered surrounding chemical waste management include transport, procurement, occupational safety, use and disposal of hazardous materials and pollution prevention, all of which can incur significant costs. It is therefore recommended that governmental ministries develop laws specifying that where possible, waste should be recycled and/or reused.

This legislation should include:

- Responsibility for the use and disposal of a product
- Responsibilities of the producer (take-back obligations)
- Planning responsibility

The user of chemicals must also bear responsibility for his/her waste products. Therefore it is necessary for the user to develop a waste management system which is in line with the applicable laws of the country. Some countries, for example, prohibit the incineration of chemical waste.

Starting a waste management system

The most important **principles** of a waste management system are:

- Waste avoidance
- Waste reduction
- Waste reuse
- Waste disposal (with regard to the safety of the community and the environment)

Working with waste means taking on responsibility.

The producer of waste is responsible for its final disposal, even if he/she appointed or hired other intermediaries, companies, transporters, etc. He/she must ensure that there are no adverse health and environmental consequences of waste handling, treatment and disposal activities. Therefore he/she is obliged to select reliable routes of disposal or implement a project capable of being certified so that all the intermediate steps are documented. These documents must then be available at all times.

Universities, laboratories and research facilities striving to implement a waste management system are moving towards the achievement of a healthy and safe environment for their employees and communities.

The following steps are necessary for the **implementation** of a waste management system in laboratories:

1. Formation of a commission from the various departments of the institution
2. Nomination of a person responsible for the waste management system
3. Collection of data in order to assess the present situation by means of a questionnaire (see Appendix 1 as an example). The **questionnaire** should provide information about:
 - the types of waste expected to be encountered
 - the nature of the waste
 - the quantity of waste
 - packaging
 - internal transport
 - temporary storage
 - final disposal
4. The commission should analyze the data from the questionnaire and use it to formulate recommendations concerning the following:
 - the replacement, where possible, of hazardous substances with products which are not harmful for the environment and health and are thus easier to dispose of

- the amount of each chemical used
 - the packaging of waste chemicals
 - the collection of waste chemicals
 - internal transport
 - storage
5. Responsibilities should be delegated
 6. Developing special safety guidelines for the laboratory (see a model of safety guidelines in Appendix 2)
 7. Sensitivity to waste and training of all employees who are working in this field
 8. Regular environmental checks concerning the identification and classification of all waste according to the relevant internal directives
 9. Constant control and comparison of the amounts of the remaining waste
 10. Constant documentation of all processes
- Finally, a functioning waste management system could form the basis for an environmental management system certification according to ISO 14001.**

Chemicals recommended for use in a laboratory

Before starting work with new chemical substances, it is necessary to verify that they are not dangerous for the environment and health, and that they can be safely eliminated under the existing conditions of the country.

1. Chemicals which are not hazardous to the environment (biodegradable chemicals)

An important element of information regarding the hazardous potential of a chemical to the environment is its water pollution classification. (See Appendix 3 for examples of water pollution classifications.)

To protect water (rivers, seas, ground water, waste water or drinking water), it is necessary to assess and classify pollutants according to their water-hazardous properties. **There are administrative regulations for each of the German Water Hazard Classes:**

- 0: No hazard to waters (sometimes without classification)
- 1: Low hazard to waters
- 2: Hazardous to waters
- 3: Severely hazardous to waters

Substances from classifications 0 and 1 are biodegradable and should be preferred. When substances with classification 1 are used, they must additionally be diluted with water (1:10) before being poured into the sink.

The Globally Harmonized System (GHS) also provides information about hazards for health and the environment.

2. Chemicals which are not hazardous to health

Comprehensive information relating to the properties of a chemical substance and its hazards are contained in its Safety Data Sheet (see Appendix 4 for an example of butane's material safety data sheet [MSDS]).

Safety data sheets (SDS) or material safety data sheets (MSDS) are important components of product responsibility and are of great importance. These data sheets are intended to provide workers and emergency personnel with procedures for handling or working with that substance in a safe manner and include physical data (melting point, boiling point, flash point, etc.), toxicity, adverse health effects, first aid measures, reactivity, storage, disposal, protective equipment and spill-handling procedures for the chemicals. SDS formats can differ from country to country depending on the national requirements.

MSDSs are a widely used system for cataloguing information on chemicals, chemical compounds and chemical mixtures. Information may include instructions for the safe use and potential hazards associated with a particular material or product. These data sheets should be both available and accessible wherever chemicals are being used.

Examples for substitutions of hazardous chemicals

The following chemicals are often used in diverse contexts, although they are environmentally hazardous and/or dangerous to health. It is highly important that measures be taken to substitute these chemicals.

Substances which are hazardous to health (carcinogenic substances)

- Benzene may be substituted with toluene, xylene or d-limonene
- Ethidium bromide may be substituted with SYBR Green (Sigma-Aldrich)

Substances which are hazardous to the environment

- Trichloroethylene may be substituted with dichloromethane (because it is recyclable)
- Carbon tetrachloride may be substituted with dichloromethane

All substances which potentially pose a chemical, health and/or environmental risk must be properly classified and labelled.

Classification and Labelling of Chemicals

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is an internationally agreed-upon system, instigated in 1992 by the United Nations (but up to 2016 not yet fully implemented in many countries). It replaces the numerous national classification and labelling standards, ensuring consistent uniform criteria on a global level. This system provides the infrastructure for all countries to implement a hazard classification and communication system.

The two major elements of GHS:

1. The classification of chemical hazards according to GHS rules:
 - Physical hazards
 - Health hazards
 - Environmental hazards
 - Hazard communication

2. The communication of the hazards and precautionary information using Safety Data Sheets and labels:

- GHS Label
- GHS Safety Data Sheet (SDS)

Labels

According to GHS, the product label must contain certain prescribed information which describes the hazards associated with the product. The chemical identity, standardized hazard statements, signal words and symbols should appear on the label according to the classification of that chemical or mixture. In some cases, precautionary statements may also be required.

HCS Pictograms and Hazards










<p>Health Hazard</p>  <ul style="list-style-type: none"> • Carcinogen • Mutagenicity • Reproductive Toxicity • Respiratory Sensitizer • Target Organ Toxicity • Aspiration Toxicity 	<p>Flame</p>  <ul style="list-style-type: none"> • Flammables • Pyrophorics • Self-Heating • Emits Flammable Gas • Self-Reactives • Organic Peroxides 	<p>Exclamation Mark</p>  <ul style="list-style-type: none"> • Irritant (skin and eye) • Skin Sensitizer • Acute Toxicity (harmful) • Narcotic Effects • Respiratory Tract Irritant • Hazardous to Ozone Layer (Non-Mandatory)
<p>Gas Cylinder</p>  <ul style="list-style-type: none"> • Gases Under Pressure 	<p>Corrosion</p>  <ul style="list-style-type: none"> • Skin Corrosion/Burns • Eye Damage • Corrosive to Metals 	<p>Exploding Bomb</p>  <ul style="list-style-type: none"> • Explosives • Self-Reactives • Organic Peroxides
<p>Flame Over Circle</p>  <ul style="list-style-type: none"> • Oxidizers 	<p>Environment (Non-Mandatory)</p>  <ul style="list-style-type: none"> • Aquatic Toxicity 	<p>Skull and Crossbones</p>  <ul style="list-style-type: none"> • Acute Toxicity (fatal or toxic)

Figure 1: Labelling of Chemicals Pictogram

ACETONITRILE

EN: Highly flammable liquid and vapour. Toxic in contact with skin. Keep away from heat/sparks/open flames/hot surfaces. — No smoking. Keep container tightly closed. Grounded container and receiving equipment. Use explosion-proof electrical/ventilating/lighting/... equipment. Use only non-sparking tools. Take precautionary measures against static discharge. Wear protective gloves/protective clothing/eye protection/face protection. IF ON SKIN: Wash with plenty of soap and water IF ON SKIN (or hair): Remove/Take off immediately all — Rinse skin with water/shower. Call a POISON CENTER or doctor if you feel unwell. IF INHALED: Remove person to fresh air. If breathing is difficult, call a POISON CENTER or doctor immediately. Use only in well-ventilated places. Store locked up.

FR: Liquide et vapeurs très inflammables. Toxique par contact cutané. Tenir à l'écart de la chaleur/des étincelles/des flammes nues/des surfaces chaudes. — Ne pas fumer. Maintenir le récipient fermé de manière étanche. Mise à la terre/l'équipement électrostatique du récipient et du matériel de réception. Utiliser du matériel électrique/ventilation/d'éclairage/... antidéflagrant. Ne pas utiliser d'outils produisant des étincelles. Prendre des mesures de précaution contre les décharges électrostatiques. Porter des gants de protection/des vêtements de protection/un équipement de protection des yeux/du visage. EN CAS DE CONTACT AVEC LA PEAU: Laver abondamment à l'eau et au savon. EN CAS DE CONTACT AVEC LA PEAU (ou les cheveux): Retirer immédiatement les vêtements. Rincer la peau à l'eau/à la douche. Appeler un CENTRE ANTIPOISON ou un médecin. Si vous vous sentez mal, appelez un médecin. Ne pas utiliser dans des lieux mal ventilés. Stocker dans un endroit verrouillé.



BG: Силно запалима течност и пари. Токсичен при контакт с кожата. Да се пази от топлина/искри/открит пламък/от открити повърхности. — Топлопозването е забранено. Съхраняването е под строг контрол. Съхраняването е в добре вентилирано помещение. Използвайте само инструменти, които не произвеждат искри. Вземете предпазни мерки срещу осакатяване на статично електричество. Използвайте предпазни ръкавици/предпазно облекло/предпазни очила/предпазна маска за лице. ПРИ КОНТАКТ С КОЖАТА: Измийте обилно със сапун и вода. ПРИ КОНТАКТ С КОЖАТА (или косата): Незабавно сваляйте цялото замърсено облекло. Облейте кожата с вода/сапун и вода. При неразположение се обадете в Незабавно сваляйте цялото замърсено облекло. Използвайте само в добре вентилирано помещение. Използвайте само в добре вентилирано помещение. Да се съхранява под ключ.

DE: Flüssigkeit und Dampf leicht entzündbar. Giftig bei Hautkontakt. Von Hitze/Funken/offener Flamme/hohen Oberflächen fern halten. Nicht rauchen. Behälter dicht verschlossen halten. Behälter und zu befüllende Anlage erden. Explosionsgeschützte elektrische Betriebsmittel/Lüftungsanlagen/ Beleuchtung/... verwenden. Nur funkenfreies Werkzeug verwenden. Maßnahmen gegen elektrostatische Aufladungen treffen. Schutzhandschuhe/Schutzkleidung/Augenschutz/Gesichtsschutz tragen. BEI BERÜHRUNG MIT DER HAUT: Mit viel Wasser und Seife waschen. BEI BERÜHRUNG MIT DER HAUT (oder dem Haar): Alle kontaminierten Kleidungsstücke sofort ausziehen. Kontaminierte Kleidung abwaschen/duschen. Bei Unwohlsein: GIFTINFORMATIONSZENTRUM oder Arzt anrufen. Alle kontaminierten Kleidungsstücke sofort ausziehen. Kontaminierte Kleidung waschen. Im Brandfall: ... zum Löschen verwenden. An einem gut belüfteten Ort aufbewahren.

ACETONITRILE

C2H3N

ACE / acetic acid nitrile / cyanomethane / ethane nitrile / ethyl nitrile / methane carbonitrile / methyl cyanide

Adresse des Unternehmens

Figure 2: Acetonitrile Label

Preparation for the disposal of chemical residues in laboratories

To eliminate waste from laboratories, it is necessary to gain information about the type of substance in question.

Disposal methods will depend upon the properties of each individual residue. For example, acidic and highly toxic bases may in some cases be neutralized, diluted and (safely) discarded.

Never discard laboratory waste without being certain that the intended disposal method is safe. If no government agencies are responsible for the collection and disposal of waste from laboratories, it is recommended that waste chemicals be stored in separate standardized containers according to the class of compound.

These are the special groups for the separation of chemicals:

- Acids, organic and inorganic
- Bases, organic and inorganic
- Halogen-free organic solvents and solutions
- Halogenated organic solvents and organic solutions containing halogens
- Saline solutions with a pH between 6 and 8, both organic and inorganic
- Solid organic and inorganic waste chemicals

These should be securely packaged in plastic bottles, boxes or in the original barrels. The containers must be properly labelled in order to eliminate doubt as to the identity of the waste in question. This identification must be clear, standardized with GHS labels and legible (neither handwritten nor chemical formulas).

It is important to coordinate the classification in advance with the authorized waste disposal company – if there is one in the vicinity.

Before disposing of chemicals by authorized companies, one should aim at minimizing the production of waste. Each user must be aware of the impacts that his/her actions may have on the environment and on human

health. It is the duty of all to take precautions so that the environmental impact is minimized.

In preparation for the proper disposal of laboratory waste, containers of suitable types and sizes must be obtained for collection of each class of waste prior to disposal.

Collection containers must be made of stable material capable of being well sealed and should be stored in a well ventilated area. Selection of the place of storage will depend upon the materials in question and their risk of explosion. In order to prevent health hazards, chemical waste should only be stored temporarily and disposed of with as little delay as possible.

Examples of chemical waste disposal requirements:

- Aqueous liquids
Aqueous solutions should be diluted and adjusted to a pH between 5 and 9 to reduce the reactivity of acids or bases before being stored in precisely labelled drums for subsequent disposal. When neutralizing, caution should be taken as these chemical reactions can be dangerous (e.g. exothermic). (See Appendix 5, "Dangerous chemical reactions".)
- Liquids containing heavy metal salts
These generally require special chemical treatment before disposal both to reduce their reactivity and to reduce the volume of waste material. Heavy metals can be precipitated as their insoluble chlorides, sulfides and carbonates by treatment with hydrochloric acid, hydrogen or ammonium sulfide and ammonium carbonate, respectively. These precipitates can then be disposed of in appropriate containers. (See Appendix 6 for examples of precipitation.)
- Special metals
Mercury should be avoided or substituted if there is no company available which offers recycling. It must be stored in a separate container. Mercury from broken thermometers can be detoxified as mercury amalgam.

Some valuable metals such as silver or copper can be processed electrolytically and then sold.

- Organic solvents, chlorinated and non-chlorinated
- Laboratories working with non-chlorinated organic solvents (esters, alcohols, aldehydes and light hydrocarbons) should store these liquids in suitable contain-

ers and send them to authorized companies for recycling. These companies must be licensed in accordance with current environmental regulations.

- Chlorinated solvents should be avoided where possible or stored separately since they can produce highly toxic products, e.g. dioxins, in case of fire.

Technical possibilities for chemical waste disposal

Chemical waste products may be disposed of in the following ways:

- Chemical or physical treatment
- Disposal of solid waste in a monitored landfill
- Incineration

Chemical or physical treatment of chemicals

The purpose of treating hazardous waste is to convert it into non-hazardous material or to stabilize or encapsulate the waste in such a way that it will not leak or represent a hazard when it is finally disposed of in the environment. Stabilization or encapsulating techniques are particularly necessary for inorganic wastes, in particular those containing toxic heavy metals.

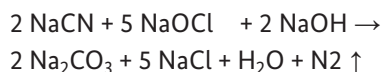
The treatment methods can be generally classified as chemical and/or physical:

Chemical methods

- Neutralization
Waste acid is neutralized with an alkali, e.g. sulfuric acid, with sodium carbonate:
$$\text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$$
- Oxidation/hydrolysis
Using common oxidizing substances such as hydrogen peroxide:
$$\text{NaCN} + \text{H}_2\text{O}_2 \rightarrow \text{NaOCN} + \text{H}_2\text{O} \uparrow$$

$$2 \text{NaOCN} + 3 \text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 \uparrow + 2 \text{NH}_3 \uparrow$$

Or sodium hypochlorite:



- Reduction
Particularly inorganic substances may be converted to a less mobile and toxic form by reduction, e.g. reducing Cr(VI) to Cr(III) by the use of ferrous(II)-sulfate:
$$\text{K}_2\text{Cr}_2\text{O}_7 + 7 \text{H}_2\text{SO}_4 + 6 \text{FeSO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 3 \text{Fe}_2(\text{SO}_4)_3$$

- Precipitation
Hazardous soluble heavy metal salts may be precipitated as their insoluble salts and subsequently safely disposed of in a landfill, e.g. the precipitation of cadmium as its hydroxide by the use of sodium hydroxide:
$$\text{CdSO}_4 (\text{aq}) + 2\text{NaOH} \rightarrow \text{Cd}(\text{OH})_2 (\text{s}) + \text{Na}_2\text{SO}_4$$

(See Appendix 6 for more examples of precipitation and Appendix 7 for more examples of chemical treatment.)

Physical methods

- Encapsulation
This involves immobilization and stabilization of hazardous materials by their incorporation within a solid matrix. For example, 25 % cement or lime plus sulfur (for better hardening) are added to the thickened solution to form a uniform paste. Ca_2SiO_4 is formed, which binds all heavy metals as CaMeSiO_4 . After four weeks, heavy metals can no longer be leached out by water. The presence of large amounts of organic substances can, however, impair this process.

Disposal of solid waste in a monitored landfill

Solid inorganic chemical waste can usually be deposited in a specially monitored landfill. This procedure is however prohibited for reactive and flammable residues due to the danger of soil contamination by the residues should leakage occur through the protective membrane. Such substances must therefore be disposed of in appropriate containers (impenetrable by air and water) according to their chemical properties in order to minimize the risk of chemical reactions.

Requirements for landfills

The disposal of chemical solid waste is carried out in properly designed and operated landfills. Controlled quantities of specific hazardous wastes may be broken down into non-hazardous substances, immobilized or adequately diluted by the physical, chemical and biochemical processes which naturally occur in landfills accepting predominantly normal municipal refuse. Such a practice is known as co-disposal and requires a certain degree of management and monitoring usually encountered only in modern regional landfills.

Types of landfills

Most refuse dumps or landfills can be classified into different categories according to the manner in which they have been designed, located and installed, particularly with regard to leachate management. Besides landfills for domestic waste, there are special types of landfills specifically designed for hazardous waste: These are authorized landfills with monitoring systems.

The location of a landfill for hazardous waste depends on technical criteria and should be decided upon only after assessment of its potential environmental impact.

A further type of landfill is that which is dedicated solely to the containment of hazardous waste over a long period of time. The hazardous waste may or may not be encapsulated before deposition in the landfill. Extra precautions must be taken to prevent leaching from rainfall and to isolate and contain the waste. This is done by incorporating at least a double membrane. At least one of these liner membranes should be a thick synthetic material, such as high density polyethylene (HDPE), which must be chemically resistant to the retained waste. Drains under-

neath and around the landfill are to be installed in order to monitor the integrity of containment over time.

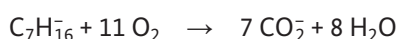
Special experience is needed when dealing with materials of doubtful identity or with products from syntheses. Long term underground storage with the possibility of later retrieval should also be considered when such materials are deposited in a landfill.

Care must be taken to ensure that the amount and type of hazardous waste is compatible with the waste previously dumped in the landfill and the resulting processes occurring.

Incineration

High temperature incineration

Incineration is the controlled combustion process used to degrade organic substances. As an example, the exhaustive combustion of the simple hydrocarbon heptane is described by the chemical reaction:



In practice, complete combustion is difficult if not impossible to achieve, but for hazardous waste, destruction or removal in excess of 99.99 % is necessary for the process to be generally acceptable.

■ Combustion parameters

Incinerators for the treatment of hazardous waste must be carefully designed and operated if they are to achieve the efficiency of destruction required. Combustion of organic materials occurs in two stages. In the primary stage, volatile matter is driven off, leaving the remainder to burn to ash. The volatile matter is combusted in the secondary stage. Incinerators are designed accordingly. High temperatures are required – for most wastes, 800–900 °C is sufficient but for materials with high thermal stability, e.g. halogenated compounds, temperatures of 1100 °C or higher may be necessary. Moreover, these temperatures must be maintained for a sufficient time period to allow complete combustion and sufficient air must be provided to supply the oxygen required for combustion. The air should be introduced in such a way that the turbulence necessary to achieve effective mixing with the combustible materials is achieved.

- Toxic combustion by-products

Public concern relating to the use of incineration for the disposal of hazardous waste relates particularly to emissions of potentially toxic combustion products from the process.

Simple examples of such emissions are:

- Carbon monoxide and hydrocarbons resulting from incomplete combustion of organic waste
- Sulfur dioxide resulting from the combustion of wastes containing sulfur
- Hydrogen chloride from the combustion of wastes containing chlorinated compounds
- Heavy metal fumes and particulates resulting from the incineration of organic wastes contaminated with heavy metals such as lead, cadmium or chromium

- Polychlorinated dibenzo dioxins and dibenzo furanes

Polychlorinated dibenzodioxins (PCDDs) and the corresponding dibenzofuranes (PCDFs) are often associated with emissions from waste incinerators. Emissions of hazardous pollutants resulting from incomplete combustion of wastes can be minimized by good incinerator design and efficient combustion practices. In the case of PCDDs and PCDFs, rapid reduction of flue gas temperatures immediately following combustion is necessary to prevent the re-formation of these compounds. Gas scrubbers using alkaline liquors are used to control acid gases such as sulfur dioxide and hydrochloric acid.

Particulate emissions, including heavy metals in the form of particles, are controlled by the use of bag filters (both wet and dry), high energy scrubbers or, less frequently, electrostatic precipitators.

High temperature incineration of organic hazardous wastes in properly designed and operating facilities can

be performed in a manner that complies with standards regulating the emission of gaseous pollutants, such as those enacted in North America and the European Community.

Potential environmental impacts:

The ash resulting from the incineration of hazardous waste may itself possess hazardous properties. This is likely to be the case when toxic heavy metals are present in the waste. The ash must therefore be constantly monitored and may require stabilization and encapsulation before disposal to landfills.

Aqueous waste materials are formed when water is used for temperature reduction of gases and/or when wet scrubbers are used for emission control. Some recycling may be possible after cooling and chemical treatment, but a quantity of liquid effluent will still need to be disposed of after appropriate treatment.

Incineration in cement factories

Furnaces used for the production of cement are designed and operated in such a way that the parameters required for the destruction of hazardous waste, as described above, are also achieved. In many countries, cement companies are officially licensed to perform the destruction of certain hazardous wastes.

Incineration in cement furnaces is particularly suitable for oily residues, solvents and residues with high calorific content and for all chemicals which are compatible with cement. It is inappropriate for organic halogens and phosphates as well as for reactive compounds.

Incineration in cement furnaces not only utilizes the calorific energy of the chemicals combusted but also the alkaline particulates present help neutralize acidic combustion products.

Technical possibilities for biological and microbiological waste disposal

This type of waste is generated in all research, teaching and environmental laboratories in which biological or microbiological agents are handled.

The four different possibilities for treatment of biological and microbiological waste are:

1. Chemical disinfection/decontamination:
2. Autoclaving
3. Kill tanks/Effluent Decontamination System (EDS)
4. Incineration

1. Chemical disinfection/ decontamination:

Disinfection is defined as the reduction of many or all disease-causing microorganisms in or on a surface or object so that they are no longer considered to be capable of transmitting disease.

Disinfection requires treatment with suitable chemicals:

Advantages

- Its simplicity
- It is relatively cheap
- Disinfectants are widely available

Disadvantages

- The chemicals used are also hazardous substances
- For proper disinfection, the correct concentrations and contact time must be followed
- The volume of waste is not reduced
- The process generates hazardous effluents which need to be further treated. (See Appendix 8, “Chemical disinfection – categories of decontaminants and their properties”.)

2. Autoclaving

This means the complete destruction or elimination of the pathogenic, reproductive or infective potential of a biological agent by use of saturated steam under pressure (e.g. 103 kPa, 121 °C, 20 min).

Advantages

- Autoclaved waste becomes safe household refuse
- Providing the correct programme is applied, all biological agents are killed
- Ecologically sound technology
- Low operating costs

Disadvantages

- Moderate to high installation costs
- Unsuitable for materials which also contain chemical or radioactive wastes
- The appearance of the waste does not change (anatomical waste, e.g. body parts!)
- The weight of the waste does not change
- Slow and time consuming

3. Kill tanks/Effluent Decontamination System (EDS)

Kill tanks are used to treat large amounts of (potentially) biologically contaminated waste water from large scale production plants, facilities for animal holding, research laboratories etc.

Potentially biologically contaminated effluents can be treated in different ways: by chemical or thermal treatment methods or a combination of both and/or pressure.

Chemical treatment: Oxidizing agents such as sodium hypochlorite and peroxyacetic acid are generally used. The oxidizing agent is mixed directly with the effluent to achieve a specified concentration, held for a specified contact time and, if required, also heated.

Advantages

- Broad-spectrum antimicrobial activity
- Simple in terms of equipment and process requirements

Disadvantages

- Specific construction materials required (corrosion!)
- Requires adequate mixing
- Solids in the system are not penetrated
- Harmful biocides or their reaction products are involved. These must be detoxified before their discharge into the environment.
- Possible release of harmful vapours or chemicals into the work area or the environment

Thermal-based treatment: combination of heat and pressure

Advantages

- Broad-spectrum antimicrobial activity
- Solids in the effluent can also be sterilized

Disadvantages

- Very expensive!
- Steam supply is needed
- High energy consumption (if not combined with a heat recovery system)
- High temperatures increase corrosion
- Pressure vessels

Thermo-chemical treatment: combination of heat and chemicals without pressure

Advantages

- Broad-spectrum antimicrobial activity
- No pressure vessel is needed
- Tank corrosion is reduced
- In comparison to thermal systems, only 10 % energy consumption
- More flexible (in case of unreliable steam supply)

Disadvantages

- Use of chemicals with all consequences (neutralization, vapour etc.)
- Adequate temperature and chemical combination has to be determined for each new step in the process

There are mainly two types of designs for liquid waste decontamination strategies: a batch operated process or a continuous process.

Batch sterilization

This is the most commonly used method. A system consisting of two or more tanks is installed, with one tank collecting waste from the facility at a time. When this tank has reached a pre-set filling level, sterilization will begin and the second tank is switched on to begin collecting further waste. Decontamination can be performed either by chemical or thermal treatment. Upon completion of sterilization, the first tank is emptied and remains idle until tank 2 is full and sterilization begins. This way, effluent collection is not interrupted by the sterilization process.

Continuous sterilization

This is similar to batch sterilization and, again, often consists of two tanks. Contaminated waste is stored until a pre-set level is reached in the tank. This then triggers the start of the process. Once the process starts, it will continue until the level of liquid in the tank is lowered to a shutdown level or the flow of contaminated effluent from the facility stops. A continuous process is a heat-based flow-through system.

4. Incineration (see page 12)

Incineration is thermal inactivation at high temperatures (200 °C to over 1000°C).

Advantages

- All microorganisms are completely destroyed
- All types of organic waste (liquid and solid) are destroyed
- Waste volumes and weight are significantly reduced (> 95 %)
- Large quantities of waste can be treated
- The waste is not recognizable post incineration

Disadvantages

- High construction costs
- Relatively high operating and maintenance costs
- Unsuitable for chemical and radioactive waste
- Incineration unsuitable for PVC or other wastes containing halogens

Transport of dangerous goods to their final disposal sites

Finally, after recycling, reuse and/or reduction in volume, the residual material must be brought to an external disposal location. For this transport, there are international regulations that are globally valid.

UN Recommendations on the Transport of Dangerous Goods

These recommendations are contained in the UN Model Regulations prepared by the Committee of Experts on the Transport of Dangerous Goods of the United Nations Economic and Social Council (ECOSOC). They cover the transport of dangerous goods by all modes of transport except by bulk tanker. They are not obligatory or legally binding for individual countries, but have gained a wide degree of international acceptance: they form the basis of several international agreements and many national laws.

“Dangerous goods” (also known as “hazardous materials”) may be pure chemical substances or mixtures. The transport hazards are grouped into nine classes, some of which are further separated into divisions and/or packing groups. The most common dangerous goods are assigned a UN number – a four digit code which identifies it internationally. Less common substances are transported under generic codes such as “UN1993: flammable liquid, not otherwise specified”.

ADR (formally, the European Agreement concerning the International Carriage of Dangerous Goods by Road) is a United Nations treaty, originally drafted in 1957, that governs the transnational transport of hazardous materials (“ADR” is derived from the French name for the treaty: *Accord européen relatif au transport international des marchandises Dangereuses par Route*). The latest version is from 1 January 2015. As of 2013, 48 states are parties to ADR.

The agreement itself is brief and simple, and its most important article is Article 2. This states that with the exception of certain exceptionally dangerous materials,

hazardous materials may in general be transported internationally in wheeled vehicles, provided that two sets of conditions are met. These conditions are described in the ADR annexes:

- Annex A regulates the merchandise involved, notably their packaging and labels.
- Annex B regulates the construction, equipment and use of vehicles for the transport of hazardous materials.

The appendices consist of nine chapters and contain the following:

- 1 General provisions: terminology, general requirements
- 2 Classification: classification of dangerous goods
- 3 Dangerous Goods List sorted by UN number, with references to specific requirements set in chapters 3 to 9; special provisions and exemptions related to dangerous goods packed in limited quantities
- 4 Packaging and tank provisions
- 5 Consignment procedures, labelling and marking of containers and vehicles.
- 6 Construction and testing of packages, intermediate bulk containers (IBCs), large packages, and tanks
- 7 Conditions of carriage, loading, unloading and handling
- 8 Vehicle crews, equipment, operation and documentation
- 9 Construction and approval of vehicles

Hazard classes

The classes of dangerous goods according to ADR are the following:

- Class 1 Explosive substances and articles
- Class 2 Gases, including compressed gases, liquefied gases and dissolved gases and vapors under pressure. They are divided into three categories:
 - Flammable gases
 - Non-flammable and non-toxic gases
 - Toxic gases (e.g. chlorine, phosgene)

- Class 3 Flammable liquids
- Class 4.1 Flammable solids, self-reactive substances and solid desensitized explosives
- Class 4.2 Substances liable to spontaneous combustion
- Class 4.3 Substances which, in contact with water, emit flammable gases
- Class 5.1 Oxidizing substances
- Class 5.2 Organic peroxides
- Class 6.1 Toxic substances
- Class 6.2 Infectious substances
- Class 7 Radioactive material
- Class 8 Corrosive substances
- Class 9 Miscellaneous dangerous substances and articles

Each entry in the different classes has been assigned a four-digit UN number. It is not usually possible to deduce the hazard class(es) of a substance from its UN number: they have to be looked up in a table. An exception to this is Class 1 substances, whose UN numbers always begin with a 0.

ADR pictograms

The ADR pictograms for chemical hazards are based on GHS Transport pictograms and non-GHS transport pictograms



1 Explosives



2.1 Flammable gases



2.2 Non-toxic/ non-flammable gases



2.3 Poison gases



3 Flammable liquids



4.1 Flammable solids



4.2 Spontaneously



4.3 Dangerous combustible when wet



5.1 Oxidizers



5.2 Organic peroxides



6.1 Poison



6.2 Infectious substances



7 Radioactive



8 Corrosive



9 Miscellaneous dangerous substances

Conclusion

The instructions of this manual have indicated what the best practices are for chemical waste management and are of general validity.

In summary:

Before commencing work with hazardous substances in a laboratory located in a developing country where legislation regarding waste disposal is lacking, it is important to obtain information about the following:

- Biodegradability and hazard to health of the substances planned to be used in the work
- Methods for substance inactivation and treatment in the laboratory
- Technical facilities for the possible disposal options in the country in question

It was decided not to include laws and regulations in this manual, since these frequently change and each country has its own specific legislation.

Author

Dr. Roswitha Meyer, born 1940 in Verden/Aller, Germany, studied pharmacy at the Eberhard Karls University of

Tübingen and received her PhD there in 1988 in organic chemistry. From 1969 to 2004 she worked as a research employee, first at the hospital pharmacy of the University Hospital and later at the Eberhard Karls University of Tübingen. Starting in 1976, she was responsible for the whole University and the University Hospital as the “Commissioner for chemical hazardous wastes and hazardous materials transportation”.

In 1993, she became a pharmacy specialist in ecology and toxicology. In 2004, she founded the environmental consulting company “MEYRO Consulting”. Since 1989, she is involved in projects for clinical and chemical waste management, organized by GIZ, PTB and the SES (Senior Expert Service), mainly in Brazil, but also in India, Chile, Paraguay, Venezuela, Honduras, Thailand, Ghana, Kenya, Tanzania and Ethiopia.

Since 2007, Dr. Meyer regularly organizes scientific seminars in Tübingen and Braunschweig for participants from Brazil, mostly from Rio/Niteroi.

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(Appendices 1–8)

Appendix 2:

A model of safety guidelines

LABORATORY REGULATIONS FOR THE ROOMS OF THE _____

(institute)

1. Areas of Application

The laboratory regulations are applicable to all laboratory rooms of _____. The regulations must be familiar to all users of the laboratory rooms and signed (contact your supervisor and the laboratory technician). New workers will be instructed by their supervisor.

2. General Fundamentals

Fundamental to the laboratory regulations are the Operational Regulations for the Handling of Solid and Liquid Hazardous Substances, which are posted in Room _____.

3. Emergency Telephone Numbers

Fire Department _____
Emergency Doctor _____
Accident Doctor _____

4. Safety Equipment

First aid lockers: position _____
Eye wash: position _____
Fume cabinets: position _____
Fire blankets: position _____
Emergency showers: position _____
Fire extinguishers: position _____

All laboratory users must make themselves familiar with the locations of safety equipment before beginning work.

5. Accidents

In the case of an accident, first aid should be administered immediately and, if necessary, the Emergency Doctor called. The following person(s) must be notified:

_____ (Tel: _____)
(supervisor)

6. Hours of Room Usage

The laboratory rooms are only to be used during working hours. Outside working hours, usage is permitted only with the approval of the laboratory supervisor (special regulations are to be followed and a member of the institute must be within calling distance). No visitors are to be allowed into the laboratory rooms since no liability exists for persons not employed by the institute.

7. Eye Protection

Safety glasses must always be worn in the laboratory.

8. Respiratory Protection

For all work involving harmful steam, gas or dust, the appropriate respiratory protection apparatus must be worn (dust masks, breathing masks). Alternatively, the fume cabinets must be used.

9. Physical Protection

Laboratory clothing must be made of a material that will not melt when heat is applied (e.g. cotton).

Laboratory coats are to be worn.

Contaminated items of clothing with must be immediately taken off and aired.

Appropriate gloves (rubber gloves, fire resistant gloves) must be worn when handling corrosive or very hot (oven) materials.

10. Fire Protection

On the outbreak of fire, the supply of gas, electricity and air should be immediately cut off. Smaller fires may be suffocated by blanketing with a wet towel. Larger fires must be fought using fire extinguishers.

Burning clothes may be extinguished with the help of the emergency showers, or better, using a fire blanket

thrown over the person (and under certain conditions by rolling on the floor).

11. Supply Connections (Gas, Water, Electricity)

All laboratory users are required to familiarize themselves with the mechanisms to turn off the water, gas and electricity.

12. Dealing with Materials which are Health Hazards

The applicable operational regulations, which are posted in _____, provide information on dealing with materials which can be hazardous to health. Directions that are important for laboratory work must be understood before the work begins and be followed.

13. Storage and Labelling

Potent poisons must be securely locked away (position: _____). All containers in which chemicals are stored must be clearly and durably labelled.

14. Pipetting by Mouth must be Completely Avoided

Pipettes with pipette balls must be used when dispensing liquids. Care must be taken when diluting concentrated acids with water: Concentrated acids should be poured in a thin stream into stirred water. Alkali hydroxides are to be added in small amounts to stirred water.

Substances which produce volatile, poisonous or otherwise hazardous gases when mixed with water, acid, alkali or other materials should not be poured down drains.

15. Large Amounts of Flammable Materials

Large amounts of flammable materials are only to be stored in the chemical store specified for this purpose (position: _____), in unbreakable containers in the security cabinets provided. Storage of these materials in corridors, stairways or hallways is forbidden.

16. Working with Flammable Materials

The heating of flammable materials without constant supervision is totally forbidden. When working with flammable material in thin walled containers, these must be protected against breakage or placed during use in safety basins filled with non-burnable adsorption material, e.g. dry sand and large enough to trap the complete contents of the containers.

17. Heavy Loads

Safety shoes must be worn in the areas where heavy experimental apparatus is lifted and moved. The laboratory technician involved must familiarize himself/herself with the operational instructions for the use of the lifting equipment.

18. High Pressure

Safety glasses are to be worn in the vicinity of apparatus under high pressure. High pressure apparatus must be fitted with excess pressure release valves, the dimensions of which are adequate to guarantee protection from bursting.

19. Laboratory-specific Instructions

Additional laboratory-specific instructions are to be followed.

20. Behaviour in Work Areas

Laboratory rooms are work rooms and not common rooms. People are not permitted to stay in the laboratories if they are not working there. Each user is responsible for cleanliness, orderliness and his/her own safety. Individual access to a work area does not rule out the possibility that several others may be using the same work area at the same time. In such cases, mutual consideration, restriction to the necessary workspace and observation of cleanliness and orderliness are especially important.

Prior to the use of equipment, it is absolutely necessary that the appropriate operating instructions are understood, or introductory guidance obtained. Damaged or defective equipment should be immediately reported.

After the completion of work, the work area and apparatus should be clean and the chemicals used must be returned to the chemical cabinet.

Before leaving the laboratory room, the windows should be closed, gas and water taps should be shut off, electronic equipment excepting permanently active (e.g. drying cabinets, refrigerators and freezers) must be turned off, the lights switched off and the laboratory locked.

Disposal of chemical waste resulting from the work is to be performed by the user according to the regulations. (See the procedures for the collection of special waste in _____). Questions should be directed to the laboratory personnel.

21. Limitations

Should legal regulations or items in other individual regulations be above those laid down in these laboratory

rules, the affected parts of the laboratory rules become invalid; the remaining part of the laboratory rules remain unaffected.

City name, _____

Signature of the manager _____

Check List:

- **Emergency Telephone Number:**
- **Emergency Doctor:**
- **Fire Department:**
- **Ambulance service:**

- Safety cabinet:
- Fume cabinet:
- Emergency shower:
- Eye wash:
- Alarm system:
- Fire extinguisher:
- Fire blanket:
- Dust mask:
- First aid lockers:
- Dry sand (non-flammable material):
- Chemical adsorption material:
- Laboratory clothing
- Eye protection and rubber gloves
- If possible, thermometer without mercury:
- Laboratory regulations about hazardous materials (MSDS):

Appendix 3:

Water pollution classification

List of some chemical substances and their German classification of water pollution (WGK)

acetone	0	potassium alum	0
active charcoal	0	potassium dichromate	3
ammonia	2	potassium ferrocyanide	1
ammonia ferrisulphate	2	potassium permanganate	2
aniline	2	resorcin	1
chromosulfuric acid	3	sodium acetate	1
di-sodium phosphate	1	sodium bisulfite	1
ethanol	0	sodium citrate	0
ferric chloride	2	sodium hydroxide	1
formaldehyde	2	sodium phosphate	1
giemsa solution	2	sodium sulfate	0
glacial acetic acid	1	sodium thiosulfate	0
hexamine (hexamethylene-tetramine)	1	sulfuric acid	1
hydrochloric acid	1	xylene	2
iodine	2		
lithium carbonate	1		
mercuric oxide	3		
methanol	1		
osmium tetroxide	3	WGK	
oxalic acid	1	0 – generally non-polluting substance	
paraffin (for histology)	0	1 – slightly polluting substance	
periodic acid	2	2 – polluting substance	
phenol (carbolic acid)	2	3 – highly polluting substance	

Methanol

Material Safety Data Sheet



MATERIAL SAFETY DATA SHEET

Methanex Corporation encourages the user of this product to read and understand the entire MSDS, and expects the user to follow the precautions specified unless the conditions of use necessitate particular procedures or methods.

1. Identification

Product Name: Methanol

CAS Number: 67-56-1

Recommended Use: Solvent, fuel, feedstock

Prepared by: TOXI.COMM INC. 5815 Plantagenet St., Montreal, QC, H3S 2K4

Revision: March 1, 2013

Product:	Methanol (CH₃OH)	EMERGENCY NUMBERS 24-hour
Synonyms:	Methanol, methyl hydrate, wood spirit, methyl hydroxide	
Company Identification:	Methanex Corporation 1800 Waterfront Centre 200 Burrard Street Vancouver, B.C. V6C 3M1 Tel. #: (604)-661-2600 Methanex Methanol Company 15301 Dallas Parkway, Ste 900 Addison, TX 75001 Tel#: (972) 702-0909	CANUTEC Emergency Tel.# (613)-996-6666 (Canada) *666 (cellular) OR CHEMTREC Emergency Tel. #: 1-800-262-8200 (Canada and USA)

2. Hazard identification

Emergency Overview

Colourless liquid, with a mild, characteristic alcohol odour when pure. Readily absorbs moisture.
Flammable liquid and vapour: Burns with a clean, clear flame, which is almost invisible in daylight, or a light blue flame. Can decompose at high temperatures forming carbon monoxide and formaldehyde. Confined space hazard.

Toxic: May be harmful if inhaled, absorbed through the skin or swallowed. Mild central nervous system depressant. May cause headache, nausea, dizziness, drowsiness, and incoordination. Severe vision effects, including increased sensitivity to light, blurred vision, and blindness may develop following an 8-24 hour symptom-free period. Coma and death may result.

Irritant: Causes eye irritation.

Possible teratogen/embryotoxin: May harm the unborn child, based on animal information.

OSHA Hazard Communication Standard

This product is a "Hazardous Chemical" as defined by the OSHA Hazard Communication Standard, 29 CFR 1910.1200.

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**Potential Health Effects**

Inhalation: Causes mild central nervous system (CNS) depression with nausea, headache, vomiting, dizziness, incoordination and an appearance of drunkenness. Metabolic acidosis and severe visual effects can occur following an 8-24 hour latent period. Coma and death, usually due to respiratory failure, may occur if medical treatment is not received. Visual effects may include reduced reactivity and/or increased sensitivity to light, blurred, double and/or snowy vision, and blindness.

Eye Contact: Moderate eye irritant.

Skin Contact: In general, primary alcohols such as methanol are not considered to be irritant to the skin. Repeated or prolonged exposure to methanol may cause dry, itchy, scaling skin (dermatitis).

Skin Absorption: Can be absorbed through the skin and cause harmful effects as described in "Inhalation" above.

Skin Sensitization: Not considered to be a sensitizer.

Respiratory Sensitization: Not considered to be a sensitizer

Ingestion: There have been reports of accidental or intentional ingestion of methanol although ingestion is not a typical route of occupational exposure. Ingestion of as little as 10 ml of methanol can cause blindness and 30 ml (1 ounce) can cause death if victim is not treated. Ingestion causes mild central nervous system (CNS) depression with nausea, headache, vomiting, dizziness, incoordination and an appearance of drunkenness. Metabolic acidosis and severe visual effects can occur following an 8-24 hour latent period. Coma and death, usually due to respiratory failure, may occur if medical treatment is not received. Visual effects may include reduced reactivity and/or increased sensitivity to light, blurred, double and/or snowy vision, and blindness.

Birth Defects/Developmental Effects: has caused teratogenic and fetotoxic effects, in the absence of maternal toxicity in animal studies.

Reproductive Effects: Not considered a reproductive toxin.

3. Composition/information on ingredients

Component	CAS #	Amount%
Methanol	67-56-1	99-100

4. First-aid measures

Inhalation: Methanol is toxic and flammable. Take proper precautions to ensure your own safety before attempting rescue (e.g. wear appropriate protective equipment and remove any sources of ignition). Remove source of contamination or move victim to fresh air, provide oxygen therapy if available. Immediately transport victim to an emergency care facility.

Skin Contact: Avoid direct contact. Wear chemical protective clothing, if necessary. As quickly as possible, remove contaminated clothing, shoes and leather goods (e.g. watchbands, belts). Immediately flush with lukewarm, gently flowing water for 15-20 minutes. Immediately obtain medical attention. Completely decontaminate clothing, shoes and leather goods before re-use or discard.

Eye Contact: Avoid direct contact. Wear chemical protective goggles, if necessary. Immediately flush the contaminated eye(s) with lukewarm, gently flowing water for 15-20 minutes, while

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holding the eyelid(s) open. If a contact lens is present, **Do not** delay irrigation or attempt to remove the lens until flushing is done. Take care not to rinse contaminated water into the unaffected eye or onto the face. Immediately obtain medical attention.

Ingestion: Never give anything by mouth if victim is rapidly losing consciousness, is unconscious or convulsing. Have victim rinse mouth thoroughly with water. **Do not induce vomiting.** If vomiting occurs naturally, have victim rinse mouth with water again. Quickly transport victim to an emergency care facility.

First Aid Comments: Provide general supportive measures (comfort, warmth, rest). Consult a physician and/or the nearest Poison Control Centre for all exposures.

All first-aid procedures should be periodically reviewed by a physician familiar with the material and its conditions of use in the workplace.

Note to Physicians: The severity of outcome following methanol ingestion may be more related to the time between ingestion and treatment, rather than the amount ingested. Therefore, there is a need for rapid treatment of any ingestion exposure. Both ethanol and fomepizole are effective antidotes for methanol poisoning, although fomepizole is preferred.

5. Fire-fighting measures

Suitable Extinguishing Media: Synthetic Fire fighting foam AR-FFF (3% solution), carbon dioxide, dry chemical powder, water spray or fog. Water may be effective for cooling, diluting, or dispersing methanol, but may not be effective for extinguishing a fire because it will not cool methanol below its flash point. Fire-fighting foams, such as multipurpose alcohol-resistant foams, are recommended for most flammable liquid fires. If water is used for cooling, the solution will spread if not contained. Mixtures of methanol and water at concentrations greater than 20% methanol can burn.

Special Hazards Arising from the Chemical

Hazardous Combustion Products: During a fire, carbon monoxide, carbon dioxide and irritating and toxic gases such as formaldehyde may be generated.

Unusual Fire and Explosion Hazards: Can accumulate in confined spaces, resulting in a toxicity and flammability hazard. Closed containers may rupture violently and suddenly release large amounts of product when exposed to fire or excessive heat for a sufficient period of time. Flame may be invisible during the day. The use of infrared and or heat detection devices is recommended.

Advice for Firefighters

Fire-Fighting Procedures: Evacuate area and fight fire from a safe distance or protected location. Approach fire from upwind. Cool fire-exposed containers, tanks or equipment by applying hose streams.

Special Protective Equipment for Firefighters: Full face, positive pressure, self-contained breathing apparatus (NIOSH approved or equivalent) or airline and appropriate chemical protective fire-fighting clothing.

NOTE: The use of cartridge masks is NOT recommended.

6. Accidental release measures

Personal Precautions, Protective Equipment and Emergency Procedures: Restrict access to area until completion of cleanup. Ensure cleanup is conducted by trained personnel only. Wear adequate personal protective equipment. Extinguish or remove all sources of ignition. Notify government occupational health and safety and environmental authorities.

Methods and Materials for Containment and Cleaning up: Do not touch spilled material. Prevent material from entering sewers, waterways or confined spaces. Stop or reduce leak if safe to do so. Contain spill with earth, sand, or absorbent material which does not react with spilled

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material. Remove liquid by intrinsically safe pumps or vacuum equipment designed for vacuuming flammable materials (i.e. equipped with inert gases and ignition sources controlled). Place in suitable, covered, labelled containers.

SMALL SPILLS: Soak up spill with absorbent material which does not react with spilled chemical. Put material in suitable, covered, labelled containers. Flush area with water.

Contaminated absorbent material may pose the same hazards as the spilled product.

LARGE SPILLS: If necessary, contain spill by diking. Alcohol resistant foams may be applied to spill to diminish vapour and fire hazard. Collect liquid with explosion proof pumps.

7. Handling and storage

Precautions for Handling: No smoking or open flame in storage, use or handling areas. Use explosion proof electrical equipment. Ensure proper electrical grounding and bonding equipment procedures are in place.

Storage: Store this material in a cool, dry, well-ventilated area away from oxidizing materials and corrosive atmospheres, in a fireproof area. Keep amount in storage to a minimum.

Storage area should be clearly identified, clear of obstruction and accessible only to trained and authorized personnel. It is recommended that storage procedures be evaluated using NFPA 70E standard and NFPA 497 practice. Do not store below ground level, or in confined spaces. Have appropriate fire extinguishers and spill cleanup equipment in or near storage area. Store away from strong oxidizers, mineral acids and metals. See Section 10, **Stability and reactivity** for more information.

Ground and bond all containers and storage vessels. Store away from heat and ignition sources and out of direct sunlight. Post storage area as a "No Smoking" area.

8. Exposure controls/personal protection

Exposure Limits

ACGIH

Time-Weighted Average (TLV-TWA): 200 ppm - Skin

Short-Term Exposure Limit (TLV-STEL): 250 ppm - Skin

TLV Basis - Critical Effect(s): Headache;
Eye damage;
Dizziness;
Nausea

Personal Protection

Eye/face Protection: Chemical safety goggles. A face shield may also be necessary.

Skin Protection: Chemical protective gloves, coveralls, boots, and/or other chemical protective clothing. Safety shower/eye-wash fountain should be readily available in the immediate work area.

Hand protection: Butyl or Viton®. Since methanol is recognized as a skin absorption hazard, check with glove manufacturers for appropriate glove material, thickness and resistance to breakthrough.

Respiratory Protection: Respiratory protection should be worn when there is a potential to exceed the exposure limit requirements or guidelines. Use an approved positive-pressure full-face self-contained breathing apparatus or a full-face supplied air respirator. The person wearing the respirator should be medically approved, fit tested and trained to operate the breathing apparatus.

Engineering Controls

Ventilation: Engineering methods to control hazardous conditions are preferred. Methods include

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mechanical (local exhaust) ventilation, process or personnel enclosure and control of process conditions. Administrative controls and personal protective equipment may also be required. Because of the high potential hazard associated with this substance, stringent control measures such as enclosure (closed handling systems) should be considered. To reduce the fire/explosion hazard, consider the use of an inert gas in the process system. Use approved explosion-proof equipment and intrinsically safe electrical systems in areas of use. For large-scale operations, consider the installation of leak and fire detection equipment along with a suitable, automatic fire suppression system. Use a non-sparking, grounded, ventilation system separate from other exhaust ventilation systems. Exhaust directly to the outside. Supply sufficient replacement air to make up for air removed by exhaust system.

9. Physical and chemical properties

Appearance: Liquid, clear, colourless

Odour: Mild characteristic alcohol odour

Odour Threshold: detection: 4.2 - 5960 ppm
(geometric mean) 160 ppm
recognition: 53 – 8940 ppm
(geometric mean) 690 ppm

pH: Not applicable

Freezing Point: -97.8°C

Boiling Point: 64.7°C

Boiling Range: Not determined

Flash Point: 11.0°C

Solubility: Completely soluble

Partial Coefficient: Log P (oct) = -0.82

Vapour Pressure: 12.8 kPa @ 20°C

Viscosity: 0.3 cP @ 25°C

Upper Explosive Limit (UEL): 36.5 %

Lower Explosive Limit (LEL): 6%

Auto Ignition Temperature: 464°C

Solvent Solubility: Soluble in all proportions in ethanol, benzene, other alcohols, chloroform, diethyl ether, other ethers, esters, ketones and most organic solvents

Critical Temperature: 239.4°C

Specific Gravity: 0.791-0.793 @ 20°C

Evaporation Rate: 4.1 (n-butyl acetate =1)

Vapour Density: 1.105 @ 15°C (air = 1)

Decomposition Temperature: Not determined

Sensitivity to Impact: No

Sensitivity to Static Charge: Low

Percent Volatility: 100

10. Stability and reactivity

Chemical Stability: Stable as supplied.

Possibility of Hazardous Reactions: Polymerisation will not occur

Conditions to Avoid: Heat, open flames, static discharge, sparks and other ignition sources.

Incompatible Materials: Avoid contact with strong oxidizers, strong mineral or organic acids, and strong bases. Contact with these materials may cause a violent or explosive reaction.

Methanol is not compatible with gasket and O-rings materials made of Buna-N and Nitrile.

Methanol is corrosive to type 12L14 carbon steel at room temperature and type 3003 aluminum,

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copper (10-100% methanol solution) and admiralty brass, at 93 deg C. Methanol is not corrosive to most metals.

Methanol attacks some forms of plastic, rubber and coatings.

Hazardous Decomposition Products: Decomposes on heating to produce carbon monoxide and formaldehyde.

11. Toxicological information

Acute toxicity

Ingestion

LD50 (oral, rat): 5600 mg/kg

LD50 (oral, rabbit): 14200 mg/kg

Dermal

LD50 (dermal, rabbit): 15800 mg/kg

Inhalation

LC50 (rabbit): 81000 mg/m³/14h

LC50 (rat): 64000 ppm/4h

Eye Damage/Irritation

Moderate eye irritant.

Skin Corrosion/Irritation

Not considered to be an irritant.

Sensitization

Not considered to be a sensitizer.

Repeated Dose Toxicity

No relevant data found

Chronic Toxicity and Carcinogenicity

Not listed by IARC, NTP, ACGIH OR OSHA as a carcinogen.

Teratogenicity, Embryotoxicity and/or Fetotoxicity

Methanol has produced fetotoxicity in rats and teratogenicity in mice exposed by inhalation to high concentrations that did not produce significant maternal toxicity.

Reproductive Toxicity

Not considered to be a reproductive toxin.

Mutagenicity

There is insufficient information available to conclude that methanol is mutagenic.

12. Ecological information

LC50 (96h, fish): 15400 -29400 mg/l

EC50 (48h, daphnia): > 10000 mg/l

EC50 (72h, algae): 22000 mg/l *Selenastrum carpicornutum* (*Pseudokichnerela subcapitata*)

Persistence and degradability

Readily biodegradable

Bioaccumulation

Does not bioaccumulate. Partition coefficient: n-octanol/water 0.77

Mobility in Soil

Mobile in soils

PBT/vPvB

Methanol**Material Safety Data Sheet**

This substance is not considered to be persistent, bioaccumulating nor toxic (PBT). This substance is not considered to be very persistent nor very bioaccumulating (vPvB).

Terrestrial Fate

The mobility of methanol in the subsurface will not be significantly limited by adsorption. Sorption of methanol to organic carbon in soil will be minor, and methanol will tend to remain in soil pore water.

Aquatic Fate

Methanol is completely miscible with water. Accordingly, its mobility in the subsurface will not be limited by solubility. Methanol has been shown to undergo rapid biodegradation in a variety of screening studies using sewage seed and activated sludge inoculum, which suggests that biodegradation will occur in aquatic environments where the concentration does not inhibit bacterial activity.

Atmospheric Fate

Methanol has a vapour pressure of 127 mm Hg at 25°C and is expected to exist solely as a vapour in the ambient atmosphere. Vapour-phase methanol is degraded in the atmosphere by reaction with photo chemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 17 days.

Other Adverse Effects

Do not flush into surface water or sanitary sewer system.

13. Disposal considerations

Review federal, provincial or state, and local government requirements prior to disposal. Store material for disposal as indicated in Section 7, **Handling and storage**. Disposal by controlled incineration or by secure land fill may be acceptable.

Recycle wherever possible. Large volumes may be suitable for re-distillation or, if contaminated, incineration. Can be disposed of in a sewage treatment facility. Methanol levels of up to 0.1% act as a food source for bacteria; above this level may be toxic to bacteria. When pumping through sewage collection systems, the level of methanol should be kept below the flammable range (a 25% methanol/water mixture is non-flammable at temperatures below 39°C). 1 ppm of methanol is equivalent to 1.5 ppm BOD loading in the sewage plant.

Container disposal

Empty containers may contain hazardous residue. Return to supplier for reuse if possible. Never weld, cut or grind empty containers. If disposing of containers, ensure they are well rinsed with water, then disposed of at an authorised landfill. After cleaning, all existing labels should be removed.

14. Transport information

Canada Transportation of Dangerous Goods (TDG):

UN Number: UN1230

Proper Shipping Name: Methanol

Hazard Class: 3(6.1)

Packing Group: II

Labels required: Flammable Liquid and Toxic

Limited Quantity: ≤ 1 litre

ERG Guide Number: 131

Methanol

Material Safety Data Sheet


**United States Department of Transport (49CFR):
(Domestic Only)**

UN Number: UN1230
 Proper Shipping Name: Methanol
 Hazard Class: 3(6.1)
 Packing Group: II
 Labels required: Flammable Liquid and Toxic
 Limited Quantity: ≤ 1 litre
 ERG Guide Number: 131

International Air Transport Association (IATA):

UN Number: UN1230
 Proper Shipping Name: Methanol
 Hazard Class: 3(6.1)
 Packing Group: II
 Labels required: Flammable Liquid and Toxic (Toxic label may be eliminated under SP 104)

International Maritime Organization (IMO):

UN Number: UN1230
 Proper Shipping Name: Methanol
 Hazard Class: 3(6.1)
 Packing Group: II
 Labels required: Flammable Liquid and Toxic
 Flash Point = 11°C
 EmS No. F-E, S-D
 Stowage Category "B", Clear of living quarters

Marine Pollutant:

No

15. Regulatory information

CANADIAN FEDERAL REGULATIONS
Hazardous Products Act Information: CPR Compliance

This product has been classified in accordance with the hazard criteria of the Canadian Controlled Products Regulations (CPR) and the MSDS contains all the information required by the CPR.

WHMIS Classification

B2 - Flammable and combustible material - Flammable liquid
 D1B - Poisonous and infectious material - Immediate and serious effects - Toxic
 D2A - Poisonous and infectious material - Other effects - Very toxic
 D2B - Poisonous and infectious material - Other effects - Toxic

CEPA, Domestic Substances List

Methanol is listed on the Domestic Substances List.

WHMIS Ingredient Disclosure List

Listed at 1%

UNITED STATES REGULATIONS

Methanol

Material Safety Data Sheet



29CFR 1910.1200 (OSHA):	Hazardous
40CFR 116-117 (EPA):	Hazardous
40CFR 355, Appendices A and B:	Subject to Emergency Planning and Notification
40CFR 372 (SARA Title III):	Listed
40CFR 302 (CERCLA):	Listed
TOXIC SUBSTANCES CONTROL ACT (TSCA):	Listed in the inventory
CALIFORNIA SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986:	Not listed
OEHHA/CALIFORNIA Title 27, Sec. 25306:	Listed

16. Other Information

Hazard Rating System

NFPA	Health	Fire	Reactivity
	1	3	0

References:

1. International Programme on Chemical Safety, Methanol, Environmental Health Criteria, World Health Organization 1997
2. Patty's Industrial Hygiene and Toxicology, 5th Edition
3. Fire Protection Guide to Hazardous Materials, 13th Edition
4. Lanigan, S., Final report on the Safety Assessment of Methyl Alcohol, International Journal of Toxicology., Volume 20, Supplement 1 (2001)
5. Forsberg, K., Quick Selection Guide to Chemical Protective Clothing
6. Nelson, B.K., Teratological assessment of Methanol and Ethanol at high inhalation levels in rats, Fundamental and Applied Toxicology, Volume 5
7. NIOSH Guide to Chemical Hazards
8. Hazardous Substance Data Base (HSDB)
9. CCOHS Cheminfo.
10. RTECS

Original Preparation Date: September 22, 2005

Disclaimer: The information above is believed to be accurate and represents the best information currently available to us. Users should make their own investigations to determine the suitability of the information for their particular purposes. This document is intended as a guide to the appropriate precautionary handling of the material by a properly trained person using this product.

Methanex Corporation and its subsidiaries make no representations or warranties, either express or implied, including without limitation any warranties of merchantability, fitness for a particular purpose with respect to the information set forth herein or the product to which the information refers. Accordingly, Methanex Corp. will not be responsible for damages resulting from use of or reliance upon this information.

This Material Safety Data Sheet may not be changed, or altered in any way without the expressed knowledge and permission of Methanex Corporation.

MSDS version: 2.0

Revisions: Revised and re-issued March 1, 2013

Appendix 5:

Dangerous chemical reactions

Chemicals	possible danger ex = explosion, ga = gasproduction, he = heat production, ig = ignition
acetaldehyde,+ acetic acid	he (polymerisation)
Acetone + chloroform	ex
Acetone + nitric acid	ig
Acetonitrile + heat	production of hydrocyanic acid
acetonitrile + nitric acid	production of hydrocyanic acid
Acrylamide + sulfuric acid	he (polymerisation)
Alcohol + perhydrol	ig/ex
Ammonia + chrome trioxide	ig/he
Ammonia + silver nitrate	ex
ammonium chloride + ammonium nitrate	ex
ammonium nitrate + sodium nitrate	ex
Aniline + oxidation	ex
Benzene + nitric acid	ex
bromine + ethyl alcohol	he
cyanogen bromide + alkali hydroxide or acids	ex
chrome sulphuric acid + acetic acid	he/ex
dichloromethane + nitric acid	he/ex(peroxide)
dimethyl sulphoxide + iron nitrate	ex
dioxan + oxidation	he
acetic acid + chrome trioxide	he/ex
acetic acid + perchloric acid	he/ex
acetic anhydride +acids	he/ex
ethyl alcohol + perhydrol	ex
ethyl alcohol + chrome trioxide	ig

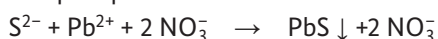
Chemicals	possible danger ex = explosion, ga = gasproduction, he = heat production, ig = ignition
formaldehyde + nitric acid	he/ga/ex
formaldehyde + perhydrol	ex
Iodine + ammonia	ex
potassium cyanide + potassium nitrate	ex
potassium dichromate +acetic anhydride	ex
potassium iodide + ammonia	ex
methyl alcohol + perchloric acid	ex
methyl alcohol + perhydrol	ex
methyl alcohol + nitric acid	ex
sodium acetate + potassium nitrate	ex
sodium hydroxide + chloroform/acetone	ex
sodium hydroxide + silver nitrate	ex
oxalic acid + silver	ex
perchloric acid	many reactions
peroxides	many reactions
phenol +formaldehyde	he/ex
picric acid + heavy metals	ex
Propanol + nitric acid	he/ex
Mercury + ammonia	ex
mercuric nitrate + ethyl alcohol	ex
nitric acid	many reactions
sulfuric acid	many reactions
silver nitrate +ammonia + methyl alcohol	ex
silver nitrate + sodium hydroxide	ex
silver nitrate + ethyl alcohol	ex
perydrol	many reactions
xylene + nitric acid	he/ex

Appendix 6:

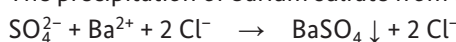
Examples of precipitation

Hydrochloric acid, hydrogen sulfide, ammonium sulfide and ammonium carbonate can produce insoluble chlorides, sulfides and carbonates of heavy metals.

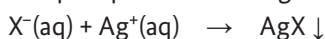
1. The precipitation of lead sulfide from lead salt solution:



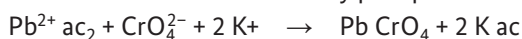
2. The precipitation of barium sulfate from barium salt solution:



3. The precipitation of halogenides such as chloride, bromide, iodide with silver:



4. The elimination of chromate by precipitation of lead chromate after adding a solution of lead acetate:



	Reagents	Precipitation
Bromide ions	Silver nitrate	Silver bromide $Ag^+ + Br^- \rightarrow AgBr \downarrow$
Iodide ions	Silver nitrate	Silver iodide $Ag^+ + I^- \rightarrow AgI \downarrow$
Chloride ions	Silver nitrate	Silver chloride $Ag^+ + Cl^- \rightarrow AgCl \downarrow$
Sulfide ions	Lead nitrate	Lead sulfide $Pb^{2+} + S^{2-} \rightarrow PbS \downarrow$
Carbon dioxide	Calcium hydroxide Barium hydroxide	Calcium carbonate $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow$ Barium carbonate $Ba^{2+} + CO_3^{2-} \rightarrow BaCO_3 \downarrow$
Phosphate ions	Silver nitrate	Trisilver phosphate $3 Ag^+ + PO_4^{3-} \rightarrow Ag_3PO_4 \downarrow$
Sulfate ions	Barium chloride	Barium sulfate $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$
Sulfide ions	Lead nitrate	Lead sulfide $Pb^{2+} + S^{2-} \rightarrow PbS \downarrow$

Appendix 7:

Examples of chemical treatment

Many chemicals can be safely disposed of simply by discharging them into the sewerage system after neutralization or after other chemical treatment, in some cases even without any further treatment.

■ Treatment of water contaminated with hexavalent chromium Cr (VI)

Hexavalent chromium compounds (Cr [VI]) are highly toxic and for this reason water containing these substances must be adequately and appropriately treated before being discharged into the environment.

The most effective method of decontamination is the reduction of chromium (VI) to the less toxic trivalent chromium, Cr (III), and its subsequent precipitation. Both the precipitate and the remaining liquid phase are significantly less toxic than the original solution. The solid residue can be filtered off and, after stabilization in cement, deposited in a controlled landfill. Using this method, chromium concentrations of below 0.1 mg/l of water may be achieved.

It is recommended that laboratory tests be conducted to determine the efficiency of the process and to detect possible inhibition of the process by the presence of other contaminants in the water which would affect the exact amount of the reagents required.

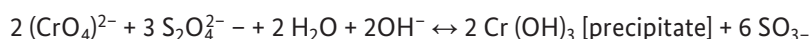
Method 1:

After the addition of sulfuric acid, sodium bisulfite (NaHSO₃) or iron sulfate (FeSO₄) is added. In a second stage, a base such as caustic soda (NaOH) is added, leading to the precipitation of chromium hydroxide.

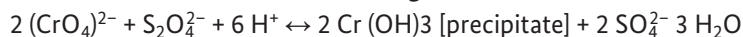
Method 2 (without adding acid):

Here, sodium dithionite (Na₂S₂O₄) is employed to both reduce chromate and precipitate the chromium as its hydroxide.

In a basic environment:

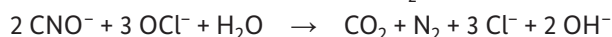
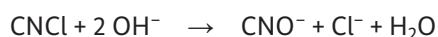
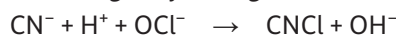


In an acidic environment and with high concentrations of chromium (I dichromate):

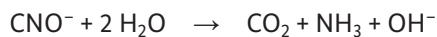
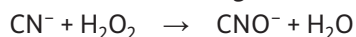


■ Decontaminating cyanide-containing solutions

Cyanide can be oxidized with sodium hypochlorite to cyanate at a pH of 10–11, and subsequently to carbon dioxide and nitrogen by adding an oxidant with a pH of 8–9.



Alternatively, cyanide can be oxidized with an approximately 5 % solution of hydrogen peroxide in an alkaline medium to form ammonia and carbon dioxide. The excess of hydrogen peroxide can be detected by means of potassium iodide starch. Undestroyed cyanide in the reaction mixture can be detected by the Prussian blue reaction. If this test is negative, then the mixture can be safely discarded.



■ Ethidium Bromide

Ethidium bromide, a powerful mutagen, is widely used in biochemical research laboratories for visualizing DNA fragments.

Aqueous solutions or gels of ethidium bromide and other materials contaminated with ethidium bromide can be detoxified using ultraviolet light (UV lamp or in the sun). Residual ethidium bromide can be readily detected on account of its fluorescence.

■ Liquid Mercury

Toxic elemental mercury can be stabilized as mercury sulfide (Hg S) by a reaction with sulfur in a sealed, temperature-controlled vacuum mixer. Mercury sulfide is non-toxic for humans, safe for the environment and can be disposed of in accordance with the applicable legislation.

■ Mercury distillation

Metallic mercury of poorer quality can be processed to reach a defined technical purity simply by distillation.

By repeated distillation in high vacuum, mercury purities of 99.99 % (4N-grade) up to 99.999999 % (8N quality) are attainable. The required purity will depend upon the intended use of the recycled mercury (physical, chemical or medical applications).

■ Osmium Tetroxide

Osmium tetroxide solutions can be converted to a less volatile (safer) form in a variety of ways, all of them involving reduction of tetroxide to the non-volatile dioxide or to a cyclic osmium (VI) ester. A freshly prepared solution of sodium sulfite (sodium sulfite slowly oxidizes to sulfate during prolonged storage) is added to a solution containing osmium tetroxide. A black or purple turbidity indicates the reduction of the tetroxide to dioxide.

Alternatively, corn oil is added to the osmium tetroxide solution and shaken. This method takes advantage of the double bonds of the unsaturated oil to form a cyclic osmic ester. The reaction may be slow since corn oil is not miscible with water, but the method is easy and effective. The solution becomes dark and a suspension will form, indicating that reaction has taken place.

Appendix 8:

Chemical disinfection – categories of decontaminants and their properties

■ Alcohols

- Ethyl or isopropyl alcohol at a concentration of 70–85 %
- Denature proteins
- Longer contact times are required when treating fungi and mycobacteria
- Variable effectiveness against non-enveloped viruses
- Not effective against bacterial spores
- Easy to use, non-corrosive
- Readily evaporated
- Extremely flammable
- Easily inactivated by organic matter, no cleansing properties

■ Formaldehyde

- Broad spectrum of activity against all classes of microorganisms
- Less susceptible to inactivation by organic material
- Prolonged contact times are required (up to 3 h against bacterial spores)
- Loss of activity at refrigeration temperatures
- Pungent, irritating odour
- Expensive
- Can cause hypersensitivity
- Low storage life

■ Phenolic compounds

- Effective against enveloped viruses
- Variable effectiveness against fungi and mycobacteria (depending on the product)
- Limited effectiveness against non-enveloped viruses
- Not effective against bacterial spores
- Toxic
- Causes skin irritation
- Unpleasant odour
- Sticky, gummy residue on treated surfaces

■ Quaternary ammonium compounds (Quats)

- Cationic detergents attach to proteins
- Strongly surface-active, therefore good surface cleaners

- Odourless
- Non-staining
- Non-corrosive to metals
- Inexpensive
- Relatively non-toxic
- Effectiveness reduced by anionic soaps and organic material (proteins)
- Ineffective against gram negative bacteria, spores, mycobacteria and many viruses

■ Hypochlorite

- Universal decontaminant against all microorganisms including bacterial spores
- Corrosive to metals
- Diluted solutions are unstable, therefore it is important to prepare fresh solutions frequently (short storage life)
- Effectiveness reduced by organic matter (protein)
- Irritation to skin and eyes

■ Glutaraldehyde

- Broad spectrum of activity against all classes of microorganisms
- Rapidly bactericidal, but requires longer contact times for mycobacteria and bacterial spores (at least 3 h)
- Non-corrosive
- Adverse health effects (mucous membrane irritation, contact dermatitis, occupational asthma)

■ Hydrogen peroxide and peroxy acids

- Broad-spectrum agent against all classes of microorganisms
- H₂O₂ can be used for the decontamination of work surfaces (laboratory benches, biosafety cabinets)
- Use of vaporized hydrogen peroxide (VHP) requires special (and expensive) equipment
- Can be corrosive to some metals (aluminium, copper, brass and zinc)
- Can decolourize fabrics, hair, skin and mucous membranes

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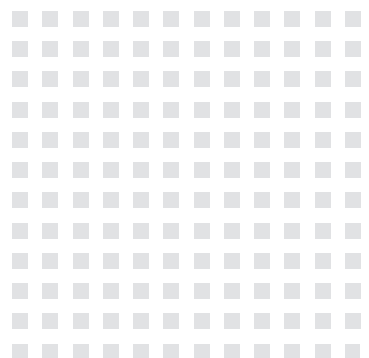
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As of January 2018





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