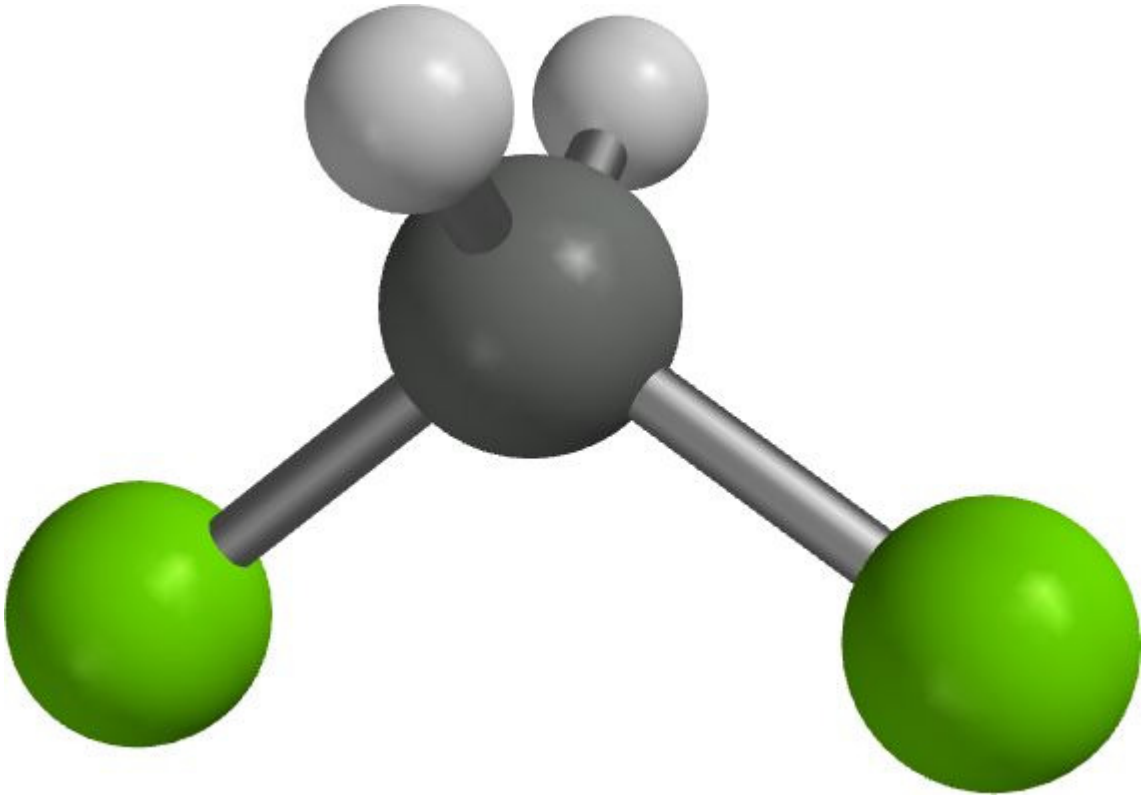
ecsa
european chlorinated solvents association

December 2015

Product Safety Summary on Dichloromethane



Methylene Chloride (Dichloromethane)

This Product Safety Summary is intended to provide a general overview of the chemical substance in the context of ICCA Global Product Strategy supported by CEFIC. The information in the summary is basic information and is not intended to provide detailed emergency response, medical or treatment information. In-depth safety and health information can be found in the (extended) Safety Data Sheet (e)SDS for the chemical substance.

GENERAL STATEMENT

Methylene Chloride, also known as Dichloromethane (DCM), is a partially chlorinated hydrocarbon of formula CH2Cl2. It is a colourless, highly volatile liquid of low toxicity to human health and environment, and it provides excellent solubility properties for a large range of organic materials, especially oils, fats, greases and resins.

It is nowadays mainly used as an industrial extraction & process solvent, mainly in the pharma industry; a small amount is used also in formulations by professionals and consumers. The low boiling point and low evaporation energy of DCM makes it well suited for recycling by distillation and enables the high efficient use of this solvent. Due to its volatility it is recommended that DCM is used in industry predominantly in closed systems by trained personnel, to keep exposure of workers below the exposure limits; in case of open systems only with appropriate technical or personal protective equipment. Uses or products with intended release of DCM (emissive uses) should either be restricted in the amounts used, and/or executed with appropriate technical and personal protective equipment to protect the health of users.

Wastes containing DCM can be fully & safely destroyed in common industrial or municipal incineration units without harmful emissions of HCl, which is either re-covered as hydrochloric acid or neutralised by milk of lime or caustic soda to give harmless inorganic salts (calcium or sodium chloride) which can be worked up or deposited with solid fly ash. However, recycling of spent DCM is recommended as much as possible to save resources and increase the overall efficiency of the solvent, therefore spent DCM should be collected and not mixed with other spent solvents, and delivered to permitted recyclers.

CHEMICAL IDENTITY

Name:	Methylene Chloride
Chemical name (IUPAC):	Dichloromethane
CAS number:	75-09-2
EC number:	200-838-9
Molecular formula:	CH_2Cl_2

Structure:

ECSA - European Chlorinated Solvent Association
Av. E. Van Nieuwenhuyse 4, box 2, B-1160 Brussels, Belgium
E-mail: ecsa@cefic.be
Web: www.chlorinated-solvents.eu

USES AND APPLICATIONS

Due to its unique solvent properties for organic substances (oils, fats, greases, waxes, resins, and almost any other organic substance) the majority of the DCM produced is used as process and extraction solvent in industry, and only a minor part is used as such or in formulations by professionals and consumers. A small fraction is used as a chemical intermediate in industry for the production of difluoromethane, also named as HFC 32 or R 32 (HFC = hydrofluorocarbon, R = refrigerant), which is used in the refrigerant blends R 407c and R410a, contained in mobile air conditioning systems.

In industry, DCM is mainly used as solvent in pharmaceuticals production including tablet coating, but also for the production of polycarbonates (plastics), cellulose acetates fibres (for yarns for textiles, cigarette filter tows and photographic films) and for production of agricultural and other fine chemicals. Minor applications include the use as foaming/ blowing agent in the production of soft polyurethane foams for mattresses and up-holstery, as solvent to extract flavours, aromas, vegetable and animal oils or fats, to decaffeinate unroasted green coffee beans and tea leafs, refining of waxes, degreasing of raw fur or raw leather, in vapour degreasing of metal parts (metal cleaning or metal degreasing), as a low-temperature heat-transfer fluid, as cleaning agent of vessels, piping and machinery in industry, and as solvent in laboratories for analytical and research purposes.

Uses by professionals and consumers include the use as solvent in formulations, i.e. adhesives, varnishes, paints, sealants, adhesives removers, paint strippers & graffiti removers, insecticide sprays, and cleaning/degreasing fluids (cold cleaner sprays).

In contrast to other (chlorinated) solvents it is not used in dry cleaning of textiles, as the solvency power is too strong for plastic yarns.

The use of DCM based paint strippers & graffiti removers has been legally banned in the EU for consumers since 1. June 2010, and for professionals since 1. June 2012, unless a national derogation has been granted by individual member states for trained and certified professionals (only the UK has granted a derogation for trained and certified professionals).

In the EU, the use of DCM in cosmetics (hair spray) will be prohibited, following a decision of the SCCS in October 2015; in the USA, the use of DCM in aerosol cosmetic products (hair spray) is prohibited since 1989.

For more information on uses that have been safety assessed under REACH, please visit the ECSA Product & Application Toolbox.

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PHYSICAL/CHEMICAL PROPERTIES

Physical state	liquid
Colour	colourless
Odour	characteristic
Relative Density at 20 °C (water = 1)	1.325
Vapour Pressure at 20 °C	476 hPa (mbar)
Freezing temperature	95°C / 178 K
Boiling temperature	40°C /313 K
Molecular weight	84.93 g/mol
Self-ignition temperature at 1013 hPa in air	605°C / 878 K
Flash point	None *
Explosion / Flammability limits in air at 20 °C and 1013 hPa	13-22% (v/v)*
Partition coefficient n-octanol/water (Log Kow) at 20 °C and pH 7	1.25
Water Solubility at 20 °C	13.2 g/l

* Vapours of DCM are difficult to ignite: under optimum conditions of 18% (v/v) DCM vapour in air the minimum energy needed for ignition is 9,300 mJ which is some 10,000 times higher than for vapours of other common flammable solvents. Therefore DCM is not classified as flammable substance after GHS or old EU legislation.

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HEALTH EFFECTS

Human Health Safety Assessment

Effects	Result
Acute toxicity: oral/ inhalation/dermal	May cause drowsiness or dizziness (Target organ: central nervous system. Route of exposure: inhalation) The available oral and dermal LD_{50} values and the 4-h inhalation LC_{50} value are all above the classification cut-offs. DCM does not need to be classified for acute toxicity for any route of exposure.
Irritation/corrosion	Causes serious eye irritation. Under occlusive conditions it can cause skin irritation, and at high airborne concentrations respiratory tract irritation may occur.
Sensitization	Not sensitising to the skin or the respiratory tract.
Toxicity after repeated exposure: oral/ inhalation/dermal	May cause damage to organs through prolonged or repeated exposure. (Target organ: liver. Route of exposure: oral and inhalation) No evidence of adverse effects on health has been found at the workplace following occupational exposure to concentrations of up-to 100 ml/m^3 (353 mg/m^3) over several years.
Genotoxicity/ mutagenicity	Not genotoxic or mutagenic in vivo.
Carcinogenicity	Suspected of causing cancer. Sufficient evidence of causing cancer in mouse studies, but not confirmed in human (epidemiological) studies.
Toxicity for reproduction	Not toxic to reproduction.

Acute toxicity

The acute toxicity of DCM by inhalation, oral and dermal administration is low. Inhalation is the principal route of exposure as DCM is a very volatile substance. Dermal exposure to liquid DCM (usually to hands) will be rather short-lived under normal working conditions as it will rapidly evaporate from the skin. Consequently, DCM is not likely to pass the skin barrier and become bio-available under non-occlusive conditions. Based on animal studies, DCM does not need to be classified for acute toxicity for any route of exposure.

DCM can cause eye irritation if splashes get into the eyes, and under occlusive conditions skin irritation, and at high airborne concentrations respiratory tract irritation. It is not corrosive to human tissue, or sensitising to the skin or the respiratory tract.

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Repeated dose toxicity

In repeated dose toxicity studies via the oral and inhalation route the main target organ is the liver. DCM did not induce adverse effects on reproduction and did not induce developmental effects. Following chronic inhalation exposure, liver and lung tumours were found in mice but not in rats. Studies have shown that a specific type of metabolism of DCM-producing reactive intermediates that are held responsible for the liver and lung tumour formation- is expressed to a greater extent in mouse tissues than in rat, hamster or human tissues, explaining the development of liver and lung tumours in mice. In a recent evaluation by IARC in 2014, IARC classified dichloromethane as 'probably carcinogenic to humans (Group 2A)' on the basis of limited evidence in humans and on sufficient evidence of carcinogenicity in mice. IARC took into account that the specific metabolism as observed in mice could occur in humans. However, occupational studies have shown no strong or consistent finding for any site of cancer despite several studies of large occupational cohorts of workers potentially exposed to high concentrations of DCM. Moreover, DCM is not genotoxic in vivo, and detailed analysis of mouse data showed that the response in mice could not be linked to effects expected for genotoxic carcinogens.

ENVIRONMENTAL EFFECTS

As a very volatile substance, DCM is mainly emitted from emissive uses (`open uses´) into the atmosphere or into waste waters, which are usually fed to municipal or industrial waste water treatment plants which eliminate DCM virtually completely.
DCM is biodegradable in all ecosystems (it is readily biodegradable as proven by testing after OECD Guideline 301 D) and will be mineralised CO2 and chloride, and thus does not persist or accumulate in living organisms or the environment.
DCM has a half-life in air of approximately 107 days (degradation occurs by photochemical oxidation via hydroxyl radicals) and therefore it is not likely to enter the stratosphere, and in turn it has a negligible stratospheric ozone depleting potential (ODP ~ 0). The contribution of emitted DCM to acid rain and smog formation is negligible, and with a photochemical ozone creation potential (POCP) of 0.009 DCM is not a precursor of tropospheric ozone. Its contribution to global warming is also negligible due to its low global warming potential (GWP) of 8.7 (based on a 100 years horizon) in combination with its short lifetime.

Effect assessment	**Result**
Aquatic toxicity	Not be classified as harmful to the aquatic environment.

Fate and behaviour	**Result**
Biodegradation	Readily biodegradable.
Bioaccumulation potential	Not bioaccumulative.
PBT / vPvB conclusion	No PBT or vPvB properties.

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Exposure

Consumer

Consumer products containing DCM usually lead to short time exposure by inhalation of vapours; as with any chemical, inhalation of DCM vapours generally should be avoided and ventilation is advised.

Many consumer uses have been risk assessed under REACH and shown to be safe; DCM containing products can be used safely if applied according to the safety instructions provided by the product label or SDS.

Worker

Exposure may occur if DCM is used openly during re-filling, disconnecting filling lines, sampling, maintenance activities etc., or by intended emissive uses of the substance or formulated products.

As DCM is a very volatile substance, the usual route of exposure is by inhalation of the vapours. Thus exposure should be avoided by keeping DCM as much as possible in a closed system; if not possible, adequate ventilation should be applied at the workplace to keep the airborne concentration of DCM vapours below the short- or long-term OEL, preferably by exhaust extraction at points where emissions occur. If this is not sufficient, personal protective equipment needs to be applied (particularly respiratory protection) to protect workers from hazardous levels of exposure.

Dermal exposure to liquid DCM (usually to unprotected hands) will be rather short-lived under normal working conditions, as DCM will rapidly evaporate from the skin; consequently, DCM is not likely to pass the skin barrier and become bio-available under non-occlusive conditions. Any potential contact with the skin should be avoided by precautionary use of appropriate protective gloves, and safety goggles should also be worn against potential spillage into the eyes. Workers have to be instructed in the substance properties and trained in the use of appropriate technical and personal protective equipment, as required. Detailed safety information is provided via the Extended Safety Data Sheet (eSDS).

Environment

Generally, discharge of the substance and formulations to waste water should be prevented and recovered as much as possible. Waste waters containing DCM above certain levels need to be treated by industrial or municipal sewage treatment plants, to keep emissions to natural waters below the limits set by legislation.

DCM is manufactured within a closed and automated process with no intentional release of the substance but only in very limited amounts (restricted by legislation and fixed in plant permits) via unavoidable traces in off-gases and effluents, as is during the industrial use of the substance. Modern off-gas abatement techniques and waste water treatment plants are common in industrial premises, as is soil protection at plants, storage and re-filling areas.

The environmental exposure by all REACH registered uses (incl. products with intended emissions of DCM) have been assessed under REACH, showing no unacceptable risk to the environment.

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RISK MANAGEMENT RECOMMENDATIONS

Generally, release of DCM to air, soil and water and exposure of people should be avoided as much as possible by applying good work hygiene standards. Prior to use, the extended safety data sheet (eSDS) should be consulted and the detailed safety recommendations for a specific use be followed!

Industry:
Due to its high volatility, handling in closed systems is recommended as the first safety measure, e.g. by using closed loop (re)filling systems. When using DCM openly, adequate ventilation (e.g. LEV) should be present.
A task risk assessment (permit to work) should be performed prior to using DCM, and workers should to be trained in the substance properties and safe use conditions etc.
Workers should generally avoid breathing vapours of chemicals and the contact with mouth, eyes and skin, and should not eat, drink, or smoke where chemicals are handled, processed, or stored. Appropriate chemical resistant gloves and safety glasses or goggles should be worn as a precautionary measure, whenever contact to DCM is possible.
Wastes containing DCM have to be collected in suited containers, and disposed to an approved waste disposal plant; preferably, spent DCM should be collected unmixed with other solvents or wastes, and sent to permitted recyclers.

Professionals & consumers:
DCM containing products can be used safely, if applied and disposed according to the safety instructions provided by the product label or eSDS.

REGULATORY PROGRAMMES

Recent regulatory programmes and evaluation documents of DCM:

- The MAK Kommission of the German Research Society (DFG) re-evaluated DCM in 2014/2015: Dichlormethan [MAK Value Documentation in German Language, 2015] (DOI: 10.1002/3527600418.mb7509d0059) published online 6 July 2015 (no English translation available yet). BAT value under investigation.
- The International Agency on Research on Cancer (IARC) re-evaluated DCM in June 2014 (Carcinogenicity of perfluorooctanoic acid, tetrafluoroethylene, dichloromethane, 1,2-dichloropropane, and 1,3-propane sultone, DOI: http://dx.doi.org/10.1016/S1470-2045(14)70316-X; final monograph not published yet.
- An evaluation under the OECD & ICCA HPV programme was finalised in October 2011.
- DCM has been registered in the EU under REACH (Regulation (EC) 1907/2006) in 2010 as a full substance >1000 t/a (full data set), last up-date in March 2014.
- The U.S. Environmental Protection Agency (US EPA) published in 2011 a TOXICOLOGICAL REVIEW OF DICHLOROMETHANE (METHYLENE CHLORIDE) (`Tox-Review 0070').
- The European Scientific Committee on Occupational Exposure Limits (SCOEL) has published in 2009 the Recommendation from the Scientific Committee on Occupational Exposure Limits for methylene chloride (dichloromethane) (SCOEL/SUM/130).
- A toxicological profile was published by the U.S. Agency for Toxic Substances and Disease Registry in 2000 (ATSDR Tox-Profile 14), for which an addendum has been published of July 2010.
- A Risk Assessment for the Marine Environment (OSPARCOM Region - North Sea) has been published by Euro Chlor in 1999.

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- The International Agency for Research on Cancer (IARC), part of the Wold Health Organisation (WHO), has published in 1999 the IARC MONOGRAPHS ON THE EVALUATION OF CARCINOGENIC RISKS TO HUMANS, VOLUME 71, dealing inter alia with DCM.
- In 1996 the Wold Health Organisation (WHO) has published the ENVIRONMENTAL HEALTH CRITERIA 164 - Methylene Chloride.

Older documents can be retrieved on the website of the Chemical Safety Information from Intergovernmental Organizations (INCHEM) (http://www.inchem.org).

EU CLASSIFICATION AND LABELLING

The substance is subject to harmonized classification under the European Classification, Labelling and Packaging Regulation (EC) 1272/2008 ('CLP regulation', implementing the EU GHS).
Industry has adopted a broader self-classification under REACH according to the rules of the CLP regulation, as follows:

Hazard Class	Hazard No.	Hazard Statement	Pictogram
Skin corrosion / irritation Cat 2	**H315**	**Causes skin irritation**	
Serious eye damage / eye irritation Cat 2	**H319**	**Causes serious eye irritation**	
Carcinogenicity Cat 2	**H351**	**Suspected of causing cancer. Route of exposure: Inhalation**	
Specific target organ toxicity - single exposure Cat 3	**H336**	**May cause drowsiness or dizziness Affected organs: central nervous system Route of exposure: Inhalation**	

Please note that packaging labels do not contain all precautionary statements (P statements) but only the condensed set of 6 P statements. For complete details on the classification and labelling of DCM (comprising also the full set of precautionary statements and the signal word, both not listed here), consult the (e)SDS.

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CONCLUSION

Due to its unique combination of properties DCM is a useful solvent for numerous applications, stretching from industrial to also professional and consumer applications. The hazards of DCM are well known based on numerous animal and human studies as well as by decades of use in large volumes all around the globe. Use has been shown to be safe when appropriate technical and/or personal protection measures are taken, i.e. when the safety instructions provided are followed.

Contact Information

For further information on this substance please contact ECSA.
Information about applications can be found at the ECSA website http://www.chlorinated-solvents.eu/toolbox/

For information on the Global Product Strategy please see the ICCA portal: http://www.icca-chem.org/en/Home/Global-Product-Strategy/

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GLOSSARY

Acute toxicity	Harmful or dangerous effect resulting from a single exposure to a substance
Biodegradation	Decomposition or breakdown of a substance under natural conditions (actions of microorganisms etc.)
Bioaccumulation	Progressive accumulation in living organisms of a chemical substance present in the environment
Carcinogenicity	Substance causing cancer
Chronic toxicity	Adverse effect after repeated exposure to a substance
Clastogenicity	Substance that causes breaks in chromosomes
Embryotoxicity	Adverse effect on foetal health
Flash point	The lowest temperature at which vapour of the substance may form an ignitable mixture with air
Genotoxicity	Substance that causes damage to genetic material; it is a broader term and besides mutagenicity, it refers to potentially harmful effects on genetic material which are not necessarily associated with mutagenicity (such as unscheduled DNA synthesis, sister chromatid exchange, DNA strand breaks, DNA adduct formation or mitotic recombination).
GHS	Global Harmonized System of chemicals classification
Hazard	Inherent substance property bearing a threat to health or environment
Mutagenicity	Substance that causes mutation(s), i.e. permanent transmissible changes in the amount or structure of the genetic material (such as direct effect on genes, and structural and numerical changes in chromosomes)
Persistence	Refers to the length of time a compound stays in the environment, once introduced
Reproduction toxicity	Includes teratogenicity, embryotoxicity and/or adverse effects on fertility
Sensitising	May cause allergy
Sediment	Topsoil, sand and minerals washed from land into water finally forming a layer at the bottom of rivers and sea
Teratogenicity	Substance effect on foetal morphology
Vapour pressure	A measure of a substance's property to evaporate
Volatile substance	Substance that evaporates readily at ambient conditions

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ADDITIONAL INFORMATION Up to the company

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