Bromomethane

IDENTIFICATION

Bromomethane
Methylbromide
R 40 B1

ZVG No: 31600
CAS No: 74-83-9
EC No: 200-813-2
INDEX No: 602-002-00-2

CHARACTERISATION

SUBSTANCE GROUP CODE

141110 Halogenated hydrocarbons, aliphatic, saturated
148300 Bromine compounds, organic
162000 Organic gases

STATE OF AGGREGATION

The substance is gaseous.

PROPERTIES

Colour: colourless

Odour: odourless

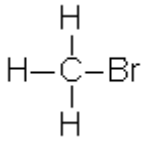
In high concentrations:
sweetish
like chloroform

CHEMICAL CHARACTERISATION

Poorly inflammable gas. Forms explosive mixtures with air.
Ignition only by ignition sources of very high energy.
The gas is easier to ignite in oxygen enriched atmosphere or in the presence of combustible air pollutants (dusts).
Moderately soluble in water.
Gas is heavier than air.
Evaporation of very cold liquid or expansion of the gas causes formation of cold mist spreading on the ground.
In gas cylinders it is present as a liquified gas.
Acute or chronic health hazards result from the substance.
The substance is hazardous to the aquatic environment.
The substance is hazardous to the ozone layer.
(see: chapter REGULATIONS).

FORMULA

CH3Br



Molar mass: 94,94 g/mol
Conversion factor (gaseous phase) at 1013 mbar and 20 °C:
1 ml/m³ = 3,95 mg/m³

TOXICOLOGY / ECOTOXICOLOGY

TOXICOLOGICAL DATA

LD50 oral rat

Value:	214 mg/kg
Reference:	Toxicology and Applied Pharmacology. Vol. 72, Pg. 262, 1984.

Reference: 02071

ECOTOXICOLOGICAL DATA

LC50 Fish (96 hours)

Minimum:	0,0008 mg/l
Maximum:	12 mg/l
Median:	5,85 mg/l
Study number:	4

Reference for median:

Canton, J.H., R.C.C. Wegman, E.A.M. Mathijssen-Spiekman, and J.Y. Wammes 1980. Hydrobiological Toxicological Research with Methylbromide. Rep.No.105/80, Natl.Inst.Public Health Environ.Hyg. :4 p.(DUT); Dawson, G.W., A.L. Jennings, D. Drozdowski, and E.

LC50 Crustaceans (48 hours)

Minimum:	2,2 mg/l
Maximum:	2,2 mg/l
Median:	2,2 mg/l
Study number:	1

Reference for median:
Canton, J.H., R.C.C. Wegman, E.A.M. Mathijssen-Spiekman, and J.Y. Wammes 1980. Hydrobiological Toxicological Research with Methylbromide. Rep.No.105/80, Natl.Inst.Public Health Environ.Hyg. :4 p.(DUT)

EC50 Crustaceans (48 hours)

Minimum:	1,7 mg/l
Maximum:	2,6 mg/l
Median:	2 mg/l
Study number:	3

Reference for median:
Canton, J.H., R.C.C. Wegman, E.A.M. Mathijssen-Spiekman, and J.Y. Wammes 1980. Hydrobiological Toxicological Research with Methylbromide. Rep.No.105/80, Natl.Inst.Public Health Environ.Hyg. :4 p.(DUT)

Reference: 02072

PHYSICAL AND CHEMICAL PROPERTIES

TRIPLE POINT

Temperature:	-93,7 °C
Pressure:	0,002 bar

MELTING POINT

Melting point:	-93,66 °C

BOILING POINT

Boiling Point:	4,0 °C

CRITICAL DATA

Crit. temperature:	194,0 °C

Crit. pressure: 52,3 bar

Crit. density: 0,577 g/cm³

DENSITY

VAPOUR DENSITY
under standard conditions (0 °C, 1013 mbar)

Value: 3,9739 kg/m³

DENSITY OF LIQUID PHASE AT BOILING POINT

Value: 1,7210 kg/l

RELATIVE VAPOUR DENSITY
Ratio of the density to dry air at the same temperature and pressure

Value: 3,36

VAPOUR PRESSURE

Vapour pressure: 1,890 bar
Temperature: 20 °C

Vapour pressure: 2,6 bar
Temperature: 30 °C

Vapour pressure: 4,9 bar
Temperature: 50 °C

FLASH POINT

Flash point: 194 °C

IGNITION TEMPERATURE

Ignition temperature: 535 °C

Temperature class: T1

Explosion group: IIA

EXPLOSION LIMITS

Lower explosion limit:
8,6 vol. %
335 g/m³

Upper explosion limit:
20 vol. %
790 g/m³

SOLUBILITY IN WATER

Concentration: 17,5 g/l

PARTITION COEFFICIENT (octanol/water)

log Kow: 1,19
Recommended value of LOG KOW Databank.

HAZARDOUS REACTIONS

Thermal decomposition:
Decomposition when heated.

Decompositon products:
hydrogen bromide
Carbonylbromide
other bromine compounds

Hazardous chemical reactions:
Risk of explosion in contact with:
alkali / alkaline earth metals
aluminium
dimethyl sulphoxide (heat)
The substance can react dangerously with:
trialkylaluminium
magnesium
metal powder
zinc
The substance forms an explosive mixture with air.

FURTHER INFORMATION

ozone depletion potential : 0,6

OCCUPATIONAL HEALTH AND FIRST AID

ROUTES OF EXPOSURE

Main Routes of exposure:
The main route for the intake for bromomethane (B.) proceed via the respiratory tract and the skin.[00083]

Respiratory tract:
The possibility of exposure exists particularly for disinfectors who can inhale B. while using it in its gaseous state.
Using volunteers exposed to 0.1 mg/m3, for inhalation through the nose 55.4 % was found to be absorbed into the blood. For inhalation through the mouth 52.1 % was

absorbed into the blood.
Studies on rats showed that for high concentrations (above about 400 mg/m3) the absorption rate decreases. At about 1000 mg/m3 it is only 27 %.[00083]

Skin:
B. is well absorbed through the intact skin. Areas with thin, gland-rich skin (axilla, groin, genital area) are penetrated extremely rapidly.
Disinfectors exposed to high vapor concentrations were poisoned in spite of using respiratory protection. This is evidence of effective skin penetration by the vapors.[00083]

Gastrointestinal tract:
Because of its low boiling point oral intake of B. is rather unlikely under realistic conditions.[99999]
For rats which received the substance in olive oil, B. was absorbed within the gastrointestinal tract, mostly without hydrolysis taking place as a first step.[00083]

TOXIC EFFECTS

Main toxic effects:
acute:
irritative to corrosive action of liquid B. to mucous membranes and skin;
concentration dependent irritating potential of vapors, toxic and lung damaging action for high concentrations[07619]
chronic:
neurotoxic and skin damaging action[99997]

Acute toxicity:
B. vapors are nearly odorless at low concentrations, sweet smelling at higher concentrations and act irritatively only at high concentrations. They show distinct local and systemic effects mostly only after a latency period of some hours, so that a warning effect is almost completely absent.[99997]
In order to reduce the extreme risk resulting, the pesticide is mixed with warning substances (eg 2 % picric chloride).[07832]
B. caused temporary eye irritation and conjunctivitis. At higher concentrations lacrimation, blurred vision, diplopia, temporary blindness and retinal bleeding occurred. Even short-term skin contact can cause irritation.[07656]
Following more intensive contact, in particular in situations such as with the liquid in gloves, in shoes or for contaminated clothing, after some time a burning sensation, deafness and (after a delay) pain were felt. After some hours blisters filled with a clear liquid, formed.[07619]
Vaporized B. in high concentrations (40 g/m3 for 40 minutes) also caused skin reddening and vesiculation. Only skin contact with the liquid or with concentrated vapors can produce poisoning with the typical symptoms (see below).
In cases of inhalative poisoning which were fatal, the following early symptoms were detectable: headache, visual disturbances, nausea, vomiting, burning of the eyes, itching, apathy, vertigo and tremor. Later cramps, fever, accelerated respiration, pale-cyanotic color of the skin and (shortly before death) confusion, manic symptoms, muscular twitching and slurring of speech appeared.[00083]

Death can be due to CNS damage (distinct brain oedema -> respiratory arrest) or formation of lung oedema.[07620]
In tests on rats, the 8h-LC50 value was 302 ppm. [99997]
The IDLH value (immediately dangerous to life or health) was reduced from 8000 mg/m3 to 1000 mg/m3 (250 ppm).[07930]
For non fatal poisoning the clinical picture is extremely different. Nearly every type of function disturbances of the CNS has been observed. A polyneuropathy syndrome frequently occurs without significant central symptoms. It is characterized by persisting numbness in the hands and legs, disturbed sensation, muscular weakness, unsteady gait and reflex disturbances. However, dyspnoea is not so strongly pronounced for less serious poisoning.[00083]
Individual cases of damage to kidneys (tubulus necrosis) and disturbances of the liver function and blood coagulation were also reported. In particular, for slight and moderate poisoning, symptoms are detectable only after a latency period of several hours. Persisting damage to the CNS was reported in single cases.[07620]

Chronic toxicity:
Chronic poisoning due to inhalation of subliminal doses for weeks or months caused severe, partially irreversible changes of the CNS. Initial symptoms were: headache, nausea, disturbance of consciousness, feeling of drunkenness, tremor, hypersensitivity of the auditory nerve, disturbance of articulation with stuttering. In addition ataxia (asynergia), vertigo with vomiting, delirium, hallucinations and sleeplessness appeared later. Furthermore, sensory disturbances and decreased visual acuity were described.[07619]
In an epidemiological study on persons exposed to B. for long time periods, dry and scaly skin was frequently detected.[99997]
A chronic exposure also produced kidney damage.[07656]
In a long-term inhalative study on rats at concentrations as low as 12 mg B./m3 histological signs of irritation to the mucous membranes of the nose were reported so that the limit value of 20 mg/m3 which is still used in some countries is too high already by that reason.[07619]

Reproductive toxicity, Mutagenicity, Carcinogenicity:
For classifying the reproductive toxicity and mutagenic and carcinogenic potential see list in Annex VI of the CLP regulation or TRGS 905 or List of MAK values.
(see section REGULATIONS).
Reproductive toxicity:
Valid animal experiments carried out to date do not give grounds to suspect a foetotoxic action.[07619]
Effects on testes tissues found in several studies on rodents are assessed to be unspecific, secondary consequences of the general toxicity.[05323]
Mutagenicity:
Certain findings in appropriate mutagenicity tests give ground for concern because of possible mutagenic action to human germ cells.
[07500]
In a series of in-vitro tests and in-vivo tests B. was found to be genotoxic.[00083]
Carcinogenicity:
There are grounds for suspecting carcinogenic potential.

This assessment takes into consideration that a part of the human population could be more sensitive to the genotoxic effects of B. than animals because of a genetically conditioned disposition (see "metabolism").[07619]
On the basis of animal experimental results available to date alone suspicion of carcinogenicity is not sufficiently established.[05323]
They furnished "limited evidence" in favor of carcinogenicity.[07980]

Biotransformation and Excretion:
After rapid establishment of equilibrium between the B. concentration in the air inhaled and in the blood, the noxa is distributed into all body compartiments.[07668]
Studies with 14C-labelled B. on rats showed that about half of the dose inhaled is exhaled as CO2. The remainder was eliminated primarily with the urine, minor amounts with the feces. Further studies made it clear that the preferential elimination pathway is dependent on the kind of application.[07620]
At higher concentrations saturation of the metabolism occurs.[07619]
An important metabolism pathway is the oxidative decomposition which proceeds via splitting off of the bromide and then via formaldehyde and formic acid to form CO2. The toxicological importance is mainly attributed to the reaction of B. with glutathione to S-methyl glutathione. The subsequent product S-methyl cysteine is able to be excreted with the urine. However, it can also be decomposed further via methane thiol and formaldehyde (elimination of formiate or further reaction to CO2). The intermediate product methane thiol is under discussion as an important cause of the neurotoxic action of B. The ability of humans to form S-methyl glutathione differs from one person to another: according to the enzyme inventory in the blood, "conjugators" and "non conjugators" are divided.[07620]
Analogous to methyl chloride, for non conjugators a lower decomposition rate (compared with animals) could cause increased sensitivity to genotoxic effects.[07619]
Alkylating properties of B. were confirmed for humans by means of detection of hemoglobin adducts formed.[99997]
The determination of adducts with serum albumin and globin was estimated to be a suitable biomonitoring parameter.
As a further parameter for the detection of exposure, the determination of bromide in the urine or blood was recommended. However, the correlation to the external exposure is relatively poor.[07620]

Annotation:
This occupational health information was compiled on 02.07.01.
It will be updated if necessary.[99999]

FIRST AID

Eyes:
Rinse the affected eye with widely spread lids for 10 minutes under running water whilst protecting the unimpaired eye.
Arrange medical treatment.

Skin:
Remove contaminated clothing while protecting yourself.
Warning: Rubber gloves do not provide safe protection.

Inhalation must be avoided (respiratory protection required).[08013]
Whilst protecting yourself, relocate the casualty away from the source of danger.
Cleanse the affected skin areas with soap under running water.
Best rinse with 5 % solution of sodium hydrogen carbonate.[08013]
Even for minor irritation or without any irritation, following extensive or prolonged skin contact, the consultation of a doctor is absolutely necessary (absorptive-toxic effects).[07656]

Respiratory tract:
Whilst protecting yourself remove the casualty from the hazardous area and take him to the fresh air.
Lay the casualty down in a quiet place and protect him against hypothermia.
In the case of breathing difficulties have the casualty inhale oxygen.
As soon as possible repeatedly have the casualty deeply breath a glucocorticoid inhalation spray in.
If the casualty is unconscious but breathing lay him in a stable manner on his side.
If the casualty has stopped breathing give mouth to nose resuscitation. If this is not possible use mouth to mouth resuscitation. Keep his respiratory tract clear.
Arrange medical treatment.

Swallowing:
Oral intake of this low boiling substance is unlikely.[80386]
Nervertheless if the liquid was ingested:[99999]
If the casualty is conscious have him drink copious amounts of liquids (water).
Under no circumstances apply cooking oil, castor oil, milk or alcohol
Arrange medical treatment.
In the case of spontaneous vomiting hold the head of the casualty low with the body in a prone position in order to avoid aspiration.[07638]

Information for physicians:
Extensive experience, mostly of inhalative poisoning of humans with bromomethane (B.) is available.[99983]
The often relatively long latency period, after which the symptoms can occur (even in the case of serious poisoning), the following are to be considered in particular.
- Symptoms of acute poisoning:
eyes: lacrimation, conjunctivitis up to cornea lesions, retinal bleeding, diplopia, temporary blindness[99997]
skin: mainly after prolonged/repeated action burning sensation, numbness, bullae;[07619] absorptive effects in particular after quasi-occlusive contact (contaminated clothing)[07798]
inhalation: minor to strong irritation, formation of a toxic lung oedema; systemic effects[00083]
ingestion: irritation for certain -> damage to mucous membranes contacted, haemorrhage, emesis; absorptive-toxic effects[99999]
absorption: neurotoxic effects (nausea, headache, vertigo, apathy, confusion; speech disturbance, psychosis, unconsciousness, from muscular twitching to generalized cramps, respiratory depression; increased irritability of the myocard;[99997] concomitant symptoms due to lung damage (tachypnoea, cyanosis);[00083] possibly

disturbances of kidney functions nephritis, tubular necrosis; disturbance of the liver function and of the blood coagulation also possible.
- Medical advice:
After eye contact with liquid or vaporized B. rinse thoroughly with a 0.5 % solution of sodium hydrogen carbonate or water. Arrange for an ophthalmologic consultation to follow for the purpose of symptomatical therapy.[99997]
Contaminated skin should be washed very carefully, if possible with a 5 % solution of sodium hydrogen carbonate. Treat damaged skin similar to burns.[08013]
Further observation of the casualty in a hospital is also indicated, and with consideration to inhalative effects which mostly occur simultaneously.[99999]
Inhalative poisoning requires continuation or the immediate start of an intensive lung oedema prophylaxis including intubation, PEEP ventilation and sedation with diazepam. Always apply glucocorticoids topically/intravenously.[07638]
Application of glucocorticoids, immobilization and aftercare (2 days) are indicated even for patients who (still) show no symptoms. Inhalation of aerosols from sodium hydrogen carbonate solution (0.5 - 2 %) or from 5 % solution of panthenol could be helpful.[08013]
Following B. inhalation a lung x-ray should be carried out in particular and as soon as possible in order to be able to optimally check the development of an oedema, possibly throughout an 8 hour period.[00330]
Infection prophylaxis is absolutely necessary.[07638]
Regular checking of the functions of the circulatory system and kidneys, of the water balance, electrolyte balance and acid-base-status must be guaranteed during the whole (protracted) course of treatment. Adrenaline and its derivatives and morphine should not be applicated. Alcohol is strictly forbidden! Strong excitation or cramps can require the application of anticonvulsants and artificial ventilation with supplementary oxygen.[08013]
After ingestion immediate, careful sucking off of stomach content (possibly after an endoscopy) should be suitable for primary poison elimination. Further treatment similar to the case of inhalation (including prophylaxis of lung oedema).[99999]

Recommendations:
Provide the physician information about the substance/product and treatment already administered.
Following poisoning with B., in recent publications N-acetyl cysteine was recommended as an antidot (initially intravenously inject 150 mg/kg bw in 200 ml 5 % glucose solution within 15 min).[07906]
Doubts regarding the effectiveness of both dimercaprol and N-acetylcysteine were registered by other authors. It was stated that there is no really suitable antidote against B. poisoning.[07798]
For the observation of possible development of neurotoxic damage following B. poisoning, the EEG was considered to be reliable.[99997]

Annotation:
This first aid information was compiled on 02.07.01.
It will be updated if necessary.

OCCUPATIONAL HEALTH CHECK

Prophylaxis offer: Occupational medical prevention has to be offered to workers conducting fumigation activities.

Deadlines: Occupational medical prevention has to be offered to employees prior to taking up work. Deadlines for the proposal of regularly recurrent occupational medical prevention are to gather from the Occupational Health Rule (Arbeitsmedizinische Regel) "AMR Nummer 2.1".

SAFE HANDLING

TECHNICAL MEASURES - HANDLING

Workplace:
Provision of very good ventilation in the working area.
The gas is heavier than air. Adequate ventilation of the floor area must be ensured as well.
Devices for detecting and reporting the presence of hazardous gases should be present.
Protect ducts and sewers against penetration by the gas.
The floor must be solvent resistant.
Eye bath required. These locations must be signposted
clearly.

Equipment:
Use only closed apparatus.
Dry apparatus by heating and/or evacuation.
Use small cylinders and place them away from working area or in an exhausting hood.
If dangerous pressure can arise from contact with heat, suitable safety measures and equipment should be provided.
If release of the substance cannot be prevented, then it should be suctioned off at the point of exit.
Consider emission limit values, a purification of waste gases if necessary.
Label containers and pipelines clearly.
There should be a shutoff for the lines at a safe distance.
Suitable materials:
For cylinders and valves:
All usual materials; exceptions see below.
Monel
Nickel
For seals:
Polytetrafluoro ethylene PTFE (Teflon)
Polychloro trifluoro ethylene PCTFE
Fluoro rubber FKM
Unsuitable materials:
Aluminium
Aluminium alloys
Risk of corrosion under moist conditions.

Advice on safer handling:
Do not store cylinders at the working area.
Do not force open valve.
When changing bottles, always inspect the leak-proof closure of the filled and empty bottles.
Refilling or transfer in storage rooms is prohibited.
Prevent cylinders from falling over.
Suck back of water into the container must be prevented. Do not allow backfeed into the container.
Use leak-proof equipment with exhaust for refilling or transfer.
Implicitly avoid any kind of exposition.
Use solvent resistant utensils.
Usually transport occurs in containers with high pressure. Use suitable equipment for the transport.
Tightly screw on the protective caps and blind nuts when transporting. Secure cylinders against falling over, do not throw.

Cleaning and maintenance:
Regular inspection of leak test required!
Only conduct maintenance and other work on or in the vessel or closed spaces after obtaining written permission.

TECHNICAL MEASURES - STORAGE

Storage:
Keep in locked storage or only make accessible to specialists or their authorised assistants.
Containers have to be labelled clearly and permanently.
Keep container below 50 deg C in a well-ventilated place.
Keep upright, protect against falling over.
Any gases that escape from storage rooms for toxic gases must be capable of being safely drawn off or collected and then disposed of. The facilities must be capable of being operated from a safe location.
Protect from exposure to sunlight.
Do not store in escape routes, work rooms, or in direct proximity to them.
For transporting, storing, preparing, emptying, and maintaining pressurized gas bottles, the detailed rules in TRG 280 must be absolutely adhered to. For pressurised gas packaging, observe the applicable TRG 300.

Conditions of collocated storage:
Storage class 2 A (Gases)
Only substances of the same storage class should be stored together.
Collocated storage with the following substances is prohibited:
- Pharmaceuticals, foods, and animal feeds including additives.
- Infectious, radioactive und explosive materials.
- Flammable liquids of storage class 3.
- Other explosive substances of storage class 4.1A.
- Flammable solid substances or desensitized substances of storage class 4.1B.

- Spontaneously flammable substances.
- Substances liberating flammable gases in contact with water.
- Strongly oxidizing substances of storage class 5.1A.
- Oxidizing substances of storage class 5.1B.
- Organic peroxides and self reactive substances.
- Combustible and non combustible acutely toxic substances of stora-ge classes 6.1A and 6.1B.
- Combustible toxic or chronically acting substances of storage class 6.1C.
- Noncombustible toxic or chronically acting substances of storage class 6.1D.
- Combustible liquids of storage class 10.

Under certain conditions the collocated storage with the following sub-stances is permitted (For more details see TRGS 510):
- Aerosols (spray bottles).
- Ammonium nitrate and preparations containing ammonium nitrate.
- Combustible corrosive substances of storage class 8A.
- Combustible solids of storage class 11.

Consider the regulations of TRG 280 at collocated storage of different compressed gases.
The substance should not be stored with substances with which ha-zardous chemical reactions are possible.

TECHNICAL MEASURES - FIRE AND EXPLOSION PROTECTION

Technical, constructive measures:
Substance is combustible.
Fire fighting equipment must be available.
Measures required by the "Explosionsschutz-Richtlinie":
- Preventing the formation of an explosive atmosphere (limiting and monitoring the concentration, making inert, sealing, ventilation, warning systems, etc.)
- Preventing the ignition of an explosive atmosphere (separation into zones, removal of sources of ignition, explosion-proof electrical installation, grounding, etc.)
- Architectural measures to limit the effects of an explosion (explosive-force-proof construction, release of explosive pressure, explosion suppression, etc.)

Protect parts of the system from any warming; if necessary, provide cooling with sprayed water.
Suitable measures must be applied to seal off waste-water systems, cable and pipe access ways, etc. (e.g.: immersing and sand beds).

Precaution on handling:
The gas-air mixture is explosive.
Area with explosion risk.
Keep at a distance from sources of ignition (e.g. electrical devices, open flames, heat sources, sparks).
Observe the smoking prohibition!
Absolutely no welding in the working area.
Only work with vessels and lines after these have been thoroughly rinsed.
Displacement with air is only permissible under strict observance of special protective measures.

It must be avoided that gases or vapours can escape into other rooms where sources of ignition are present.

ORGANISATIONAL MEASURES

Instruction on the hazards and the protective measures using instruction manual (TRGS 555) are required with signature if just more than one minor hazard was detected.
Instruction must be provided before employment and then at a minimum of once per annum thereafter.
An escape and rescue plan must be prepared when the location, scale, and use of the work-site so demand.
It must be assured that the workplace limit values are being maintained. If the limit values are exceeded, additional protection measures are necessary.
The measurements must be recorded and kept on file.
The number of employees who work with the hazardous substance must be kept to a minimum.
Observe the restrictions on juvenile employment as defined in the "Jugendarbeitsschutzgesetz".
Observe the restrictions on the employment of expectant and nursing mothers as defined in the "Mutterschutzverordnung".
Only employees are permitted to enter the work areas. Signposting to this effect must be displayed.

PERSONAL PROTECTION

Body protection:
Depending on the risk, wear gas-tight protective clothing.
Use protective boots while handling gas cylinders.

Respiratory protection:
In an emergency (e.g.: unintentional release of the substance, exceeding the occupational exposure limit value) respiratory protection must be worn. Consider the maximum period for wear.
This is a low-boiling-point substance of group 2 of the BGR 190.
Respiratory protection: Gas filter AX, colour code brown.
Max. concentration for use:
1000 ml/m³ for max. 60 min.
5000 ml/m³ for max. 20 min.
Filters may only be used in their original condition. Repeated use is permissible for the appropriate maximum period within a single shift (max. 8 hours). Do not use AX filters against mixtures of low-boiling-point substances and other organic compounds.
Use insulating device for concentrations above the usage limits for filter devices, for oxygen concentrations below 17% volume, or in circumstances which are unclear.

Eye protection:
Sufficient eye protection must be worn.
Wear chemical safety goggles.
If there is a risk of gases escaping, eye safety is best protected by wearing a full mask.

When handling liquid gas, chemical safety goggles must be used as well as a protective shield.

Hand protection:
Wear leather gloves to prevent frostbite injuries from rapidly expanding gas when handling pressurised gas bottles.
Skin protection cremes do not protect sufficiently against the substance. When there is a risk of direct contact with the substance, chemical-resistant gloves are required.

Occupational hygiene:
Avoid contact with skin. In case of contact wash skin.
Avoid contact with eyes. In case of contact rinse the affected eye(s).
Avoid inhalation of gas.
Change and air out clothing that has been in contact with or taken up any of the gas.

DISPOSAL CONSIDERATIONS

Hazardous waste according to Waste Catalogue Ordinance (AVV).
Compressed gas cylinders can normally be returned to the supplier. Pressurised cans are non-returnable and must be disposed of.
Do not empty pressure vessels to the point of pressure compensation. Mark empty vessels to avoid confusion with full ones.
Alternative:
Drop substace slowly, under stirring and cooling into a solution consisting of 10% ethanol amine, 30% diethyleneglycol monobutyl ether and 60% water.
Place in a collection container for halogen-free organic solvents and solutions of halogen-free organic substances.
Collection vessels must be clearly labelled with a systematic description of their contents. Store the vessels in a well-ventilated location. Entrust them to the appropriate authorities for disposal.

ACCIDENTAL RELEASE MEASURES

Provide adequate ventilation.
Evacuate area. Warn affected surroundings.
The hazardous area may only be entered once suitable protective measures are implemented. Only then can the hazardous situation be removed.
Wear respiratory protection, eye protection, hand protection and body protection (see chapter Personal Protection).
Attempt to stop the gas from escaping. Otherwise place leaky bottles under a suctioning device or put them outdoors.
Contain escaping gases/vapours with water.
Afterwards ventilate area.

Endangerment of watert:
Severe hazard to waters. Avoid penetration into water, drainage, sewer, or the ground.
Inform the responsible authorities about penetration of even small quantities.

FIRE FIGHTING MEASURES

Classes of fires:

C gaseous, also compressed substances

Suitable extinguishing media:

Water (spray - not splash)
Dry extinguishing powder
Carbon dioxide extinguisher with gas nozzle

Instructions:

In the case of fire advise fire fighters on the presence of gas cylinders.
Cool surrounding containers with water spray.
If possible, take container out of dangerous zone.
Heating causes a rise in pressure, risk of bursting and explosion.
Shut off sources of ignition.
Only put out fire if the gas flow can be interrupted.
Risk of explosion from gas accumulation and backfire.
Do not allow runoff to get into the sewage system.

Special protective equipment:

Attention! Hazardous decomposition products may occur.
Hydrogen bromide
Carbonyl bromide
Wear self-contained breathing apparatus and special tightly sealed suit.

REGULATIONS

Classification:

Gases under pressure, compressed gas; H280
Acute toxicity, Category 3, oral; H301
Acute toxicity, Category 3, inhalation; H331
Skin irritation, Category 2; H315
Eye irritation, Category 2; H319
Specific Target Organ Toxicity (single exposure), Category 3; H335
Germ cell mutagenicity, Category 2; H341
Specific Target Organ Toxicity (repeated exposure), Category 2; H373
Hazardous to the aquatic environment, Acute Category 1; H400
Hazardous to the ozone layer, Category 1; H420

Signal Word: "Danger"

Hazard Statement - H-phrases:
H280: Contains gas under pressure; may explode if heated.
H301+H331: Toxic if swallowed or if inhaled.
H315: Causes skin irritation.
H319: Causes serious eye irritation.
H335: May cause respiratory irritation.
H341: Suspected of causing genetic defects.
H373: May cause damage to organs through prolonged or repeated exposure.
H400: Very toxic to aquatic life.
H420: Harms public health and the environment by destroying ozone in the upperatmosphere

Precautionary Statement - P-phrases:
P261: Avoid breathing gas.
P273: Avoid release to the environment.
P281: Use personal protective equipment as required.
P301+P310: IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.
P305+P351+P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P311: Call a POISON CENTER or doctor/physician.

Manufacturer's specification by Sigma-Aldrich Group

Reference: 01221

The substance is listed in appendix VI, table 3.1 of CLP regulation.
The given classification can deviate from the listed classification, since this classification is to be complemented concerning missing or divergent danger classes and categories for the respective substance.

Reference: 99999

GHS-CLASSIFICATION OF MIXTURES

The classification of mixtures containing this substance results from Annex 1 of Regulation (EC) 1272/2008.

Reference: 07500

COLOUR CODING OF GAS CYLINDERS

Cylinder shoulder colour: Yellow
(toxic and/or corrosive gases)

WORKPLACE LABELLING ACCORDING TO GERMAN ASR A1.3

Prohibition label:

No Smoking

No admittance for unauthorized persons

No eating and drinking

Warning label:

Caution - toxic material

Caution - gas cylinder

Precept label:

Use safety goggles

Wear safety shoes

Wear safety gloves

GERMAN WATER HAZARD CLASS

Substance No: 264

WGK 3 - severe hazard to waters

Classification according to the Administrative Regulation of Substances Hazardous to Water (VwVwS)

TECHNICAL INSTRUCTIONS ON AIR QUALITY CONTROL (TA LUFT)

Chapter 5.2.5 Organic Substances, class I

The following values are in all not allowed to be exceeded in the exhaust gas:

Mass flow: 0,10 kg/hr

or

Mass conc.: 20 mg/m³

TRANSPORT REGULATIONS

UN Number: 1062
Shipping name: Methyl bromide, with not more than 2 % chloropicrin
Hazard Identification Number: 26
Class: 2.3 (Toxic gases)
Packing Group: -
Danger Label: 2.3

Special labelling: Symbol (fish and tree)

Tunnel restrictions:

Transports in tanks: passage forbidden through tunnels of category C, D und E.
Other transports: passage forbidden through tunnels of category D and E.

TRGS 900 - GERMAN OCCUPATIONAL EXPOSURE LIMIT VALUES

1 ml/m³
3,9 mg/m³

Peak limitation: Excursion factor 2
Duration 15 min, mean; 4 times per shift; interval 1 hour
Category I - Substances for which local irritant effects determine the exposure limit value, also respiratory allegens

Source: DFG

Reference: 05350

RECOMMENDATIONS OF MAK-COMMISSION

This data is recommended by scientific experience and is not established law.

1 ml/m³
3,9 mg/m³

Limitation of exposure peaks:
Excursion factor 2
Duration 15 min, mean; 4 times per shift; interval 1 hour

Risk of percutaneous absorption

Carcinogenic: Category 3B
Substances which are proved/possibly carcinogenic and therefore give reason for concern. There are clues for carcinogenic effects which however are not enough for allocation into a different category. In case there are no genetically toxical effects a MAK-value can be defined.

Pregnancy: Group C
There is no reason to fear a risk of damage to the developing embryo or foetus when MAK and BAT values are adhered to.

Reference: 08102

SEVESO III - Directive

Annex I Part 1 Section: H2
Acute toxic, Category 2 or 3 (inhalation)
Qualifying Quantity Column 2: 50 t
Qualifying Quantity Column 3: 200 t

Annex I Part 1 Section: E1
Hazardous to the aquatic environment, Category Acute 1 or Chronic 1

Qualifying Quantity Column 2:	100 t
Qualifying Quantity Column 3:	200 t

RESTRICTIONS OF USE / BANS OF USE

Regulation (EC) No 1005/2009 on substances that deplete the ozone layer
Annex I to Article 3
The production, the use and the placing on the market of this substance is prohibited.
The amount of methyl bromide produced for quarantine and preshipment application is not included in this prohibition.
Further information on the prohibition and exceptions can be taken from the regulation.

Ordinance on substances that deplete the ozone layer
In Germany some of the exceptions on the prohibitions as laid down in the regulation 2037/2000/EC do not apply.
Information on this matter can be taken from the ChemOzonSchichtV.

Second Ordinance on the Implementation of the Federal Immission Control Act
First Section, §§ 1 and 2
It is prohibited to utilise the substance in the following facilities:
- surface treatment facilities (e.g. cleaning of items and materials)
- dry cleaning facilities and textile finishing plants
- extraction facilities (e.g. extraction of flavours, fats and oils)

Further details on prohibitions and exceptions can be taken from the Second Ordinance for the Implementation of the Federal Immission Control Act.

Ordinance on Prohibitions of Use of Plant Protection Products
Attachment 2 to §§ 1, 4 and 5 Paragraph 2
The utilisation of the substance is only permissible
1. amongst others for the fumigation of mills, stockrooms
and containers for transportation against storage pests
2. for soil treatment outside of water protection areas
The application in nature protection areas and national
parks is forbidden.
Emblements, plants or culture media which is covered with or contains a plant protection product that contains the substance must not be imported.
Further information on restrictions and exceptions can be taken from the Ordinance on Prohibitions of Use of Plant Protection products.

Directives on Safety in School (BGR/GUV-SR 2003)
General ban for activities in schools.
Substance list to GUV-SR 2004 (as of 11.2010)

FURTHER REGULATIONS

TRGS 200
Einstufung und Kennzeichnung von Stoffen, Zubereitungen und Erzeugnissen;

Ausgabe Oktober 2011

TRGS 201
Einstufung und Kennzeichnung bei Tätigkeiten mit Gefahrstoffen; Ausgabe Oktober 2011

TRGS 400
Gefährdungsbeurteilung für Tätigkeiten mit Gefahrstoffen; Ausgabe Dezember 2010; geändert und ergänzt September 2012

TRGS 555
Betriebsanweisung und Information der Beschäftigten; Ausgabe Januar 2013

TRGS 600
Substitution; Ausgabe August 2008

TRGS 402
Ermitteln und Beurteilen der Gefährdungen bei Tätigkeiten mit Gefahrstoffen: Inhalative Exposition; Ausgabe Januar 2010, zuletzt geändert und ergänzt April 2014

TRGS 401
Gefährdung durch Hautkontakt, Ermittlung - Beurteilung - Maßnahmen; Ausgabe Juni 2008; zuletzt berichtigt März 2011

TRGS 407
Tätigkeiten mit Gasen - Gefährdungsbeurteilung; Ausgabe Juni 2013, berichtigt Dezember 2013

TRGS 725/TRBS 3145
Ortsbewegliche Druckgasbehälter - Füllen, Bereithalten, innerbetriebliche Beförderung, Entleeren; Ausgabe Juni 2013

TRGS 726/TRBS 3146
Ortsfeste Druckanlagen für Gase; Ausgabe April 2014

TRGS 510
Lagerung von Gefahrstoffen in ortsbeweglichen Behältern; Ausgabe Januar 2013, geändert und ergänzt November 2014

TRGS 500
Schutzmaßnahmen; Ausgabe Januar 2008, ergänzt Mai 2008

LINKS

Statement concerning the rating as carcinogenic, mutagenic or toxic for reproduction (in german only, source BAuA)
International Limit Values
OECD Screening Information DataSet (SIDS)

The MAK Collection for Occupational Health and Safety
Principles for the Safe Handling and Distribution of Highly Toxic Gases and Mixtures (IGC Doc 130/11/E)
Safe Transfer of Toxic Liquefied Gases (IGC Doc 188/14/E)
Publications of the IGV (Industriegaseverband e.V.) (in german only)
Publications of EIGA (European Industrial Gases Association) Documents Download

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Reference: 05001
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Reference: 05174
Kühn-Birett-Merkblätter: 174. Ergänzungslieferung; 06/2004

Reference: 05200
Kühn-Birett "Merkblätter Gefährliche Arbeitsstoffe" Loseblattsammlung mit Ergänzungslieferungen, ecomed Sicherheit, Landsberg

Reference: 05300
TRGS 510 "Lagerung von Gefahrstoffen in ortsbeweglichen Behältern" Ausgabe Januar 2013, geändert und ergänzt November 2014

Reference: 05323
Begründungen zur Bewertung von Stoffen der TRGS 905 stehen als Bekanntmachung des AGS unter www.baua.de/prax

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TRGS 900 "Arbeitsplatzgrenzwerte" Ausgabe Januar 2006, zuletzt geändert und ergänzt Oktober 2014, berichtigt Dezember 2014

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