

Methyl mercaptan

MAK Value Documentation, supplement – Translation of the German version from 2019

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Keywords:

methyl mercaptan, odour nuisance, maximum workplace concentration, MAK value, peak limitation

Abstract

The German Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area has re-evaluated the maximum concentration at the work place (MAK value) of methyl mercaptan [74-93-1]. Available publications and unpublished study reports are described in detail. No new data are available that would be relevant for the derivation of a MAK value for methyl mercaptan. Therefore, the MAK value of 0.5 ml/m³ is retained based on slight behavioural changes at 2 ml/m³ in a 90-day inhalation study in rats. The MAK value of 0.5 ml/m³ for methyl mercaptan is supported by a limited inhalation study with 3 volunteers exposed to ethanethiol, showing irritation and other symptoms after repeated exposure to ethanethiol in a concentration of 3.9 ml/m³, but not after 0.39 ml/m³. The behavioural changes in rats exposed to methyl mercaptan are interpreted as a result of the odour nuisance or the local irritation. Therefore, methyl mercaptan is classified in Peak Limitation Category I with an excursion factor of 1 as no studies in humans are available. In a screening study for repeated exposure and reproductive toxicity with sodium methanethiolate no foetotoxic effects were observed up to the highest dose tested of 45 mg/kg body weight, however, the teratogenicity was not examined. Methyl mercaptan remains assigned to Pregnancy Risk Group D. Skin contact is not expected to contribute significantly to systemic toxicity. There are no data on sensitization. Methyl mercaptan and sodium methanethiolate are neither mutagenic nor clastogenic.

Citation Note:

Hartwig A, MAK Commission. Methyl mercaptan. MAK Value Documentation, supplement – Translation of the German version from 2019. MAK Collect Occup Health Saf. 2020 Dec;5(4):Doc082. DOI: [10.34865/mb7493e5_4ad](https://doi.org/10.34865/mb7493e5_4ad)

Manuscript completed:
26 Apr 2018

Publication date:
21 Dec 2020

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MAK value (1969)	0.5 ml/m³ (ppm) \approx 1.0 mg/m³
Peak limitation (2018)	Category I, excursion factor 1
Absorption through the skin	–
Sensitization	–
Carcinogenicity	–
Prenatal toxicity (2000)	Pregnancy Risk Group D
Germ cell mutagenicity	–
BAT value	–
CAS number	74-93-1
Vapour pressure at 25 °C	2013 hPa (NLM 2018)
log K _{OW}	0.78 (calculated; NLM 2018)
Solubility at 25 °C	15.39 g/l water (NLM 2018)
pKa	10.33 (NLM 2018)
1 ml/m³ (ppm) \approx 1.996 mg/m³	1 mg/m³ \approx 0.501 ml/m³ (ppm)

For methyl mercaptan, documentation from 2000 (Greim 2003) and a supplement on peak limitation from 2002 (Greim 2002, available in German only) are available.

For the end points repeated toxicity, allergenicity, genotoxicity and reproductive toxicity, there are data also for sodium methanethiolate (CAS number 5188-07-8). The sodium salt of methyl mercaptan dissociates in water to form the methanethiolate anion and the sodium cation. Depending on the pH, there is a steady-state between the anion and methyl mercaptan itself (OECD 2008). Sodium methanethiolate is strongly alkaline.

Determinations in workplace air carried out between 1996 and 2002 in a production plant yielded methyl mercaptan concentrations of < 0.01 to 3 ml/m³. Only one sample exceeded the ACGIH TWA-TLV workplace limit of 0.5 ml/m³. In a second plant, all methyl mercaptan samples taken between 1997 and 2002 were between < 0.003 and < 0.49 ml/m³ and thus below the TLV, 88% were less than half the TLV. Short-term determinations of 5 to 30 minutes duration yielded values between < 0.14 and 2.5 ml/m³. The unpleasant odour of methyl mercaptan provides additional warning and avoidance of exposure (OECD 2008).

Mechanism of Action

As already described in the documentation of 2000 (Greim 2003), in the presence of suitable metal ions thiols can contribute to the formation of reactive oxygen species by means of autoxidation. The resulting disulfides can be reduced again to thiols. This redox cycling can lead to oxidative stress. Aliphatic thiols have a haemolytic effect, recognizable by the presence of Heinz bodies in the erythrocytes, which are formed by irreversibly denatured haemoglobin. As a result, the number of erythrocytes decreases as they lose their deformability and are destroyed in the reticulohistiocytic system. Erythroclasia occurs mainly in the spleen, recognizable by enlargement and dark

discoloration. A decrease in circulating erythrocytes stimulates compensatory erythropoiesis, but if too few new erythrocytes are formed this can lead to anaemia (Munday 1989).

Toxicokinetics and Metabolism

Methyl mercaptan can be absorbed by inhalation (Greim 2003). There are no studies available for the dermal absorption of methyl mercaptan. Under normal conditions, methyl mercaptan is gaseous; this means that in order to calculate the amount absorbed through the skin it must first be determined which substance concentration is present in an aqueous phase on the skin surface with exposure at the level of the MAK value. From Henry's constant H_{pc} ($0.003124 \text{ atm} \times \text{m}^3/\text{mol}$; NLM 2018) and the MAK value ($P_g = 0.5 \text{ ml/m}^3$), a concentration of $c_L = P_g / H_{pc} = 0.5 \times 10^{-6} \text{ atm} \times \text{mol} \times 10^{-3} \text{ m}^3 / 0.003124 \text{ atm} \times \text{m}^3 \times l = 1.6 \times 10^{-7} \text{ mol/l} = 7.7 \times 10^{-6} \text{ g/l}$ in an aqueous film on the skin surface is obtained. Using the mathematical models of Fiserova-Bergerova et al. (1990), Guy and Potts (1993) and Wilschut et al. (1995), dermal fluxes of $2.28 \times 10^{-7} \text{ mg/cm}^2$ and hour, $2.53 \times 10^{-8} \text{ mg/cm}^2$ and hour and $6.15 \times 10^{-8} \text{ mg/cm}^2$ and hour, respectively, can be calculated for this substance concentration. Thus, for an 8-hour activity with exposure at the level of the MAK value, and assuming exposure of the skin of the whole body ($18\,000 \text{ cm}^2$), a maximum absorbed amount of 0.03 mg can be estimated.

Animal Experiments and in vitro Studies

Subacute, subchronic and chronic toxicity

Inhalation

The current MAK value for methyl mercaptan is based on the results of a 90-day inhalation study in male Sprague Dawley rats exposed whole-body to methyl mercaptan concentrations of 0, 2, 17 or 57 ml/m^3 . A detailed description of this study and its results can be found in the documentation of 2000 (Greim 2003). As from the lowest concentration, a change in the behaviour of the animals was observed (huddling together towards the periphery of the chamber with upturned noses), which was more frequent with increasing concentration (see below). The retarded body weight gains, and thus a systemic effect, were statistically significant only in the high concentration group (American Paper Institute Inc 1980; Tansy et al. 1981). This study does not meet the requirements for a subchronic study according to the OECD test guideline, among other things because histopathological examinations were performed only on the heart, lungs, small intestine and kidneys of 5 animals. The original report of the study stated that behavioural abnormality was "suggestive" at 2 ml/m^3 , "more apparent" at 17 ml/m^3 and "markedly obvious" at 57 ml/m^3 (American Paper Institute Inc 1980).

Oral administration

There are no studies with oral administration of methyl mercaptan. Two 14-day range-finding studies and one screening study carried out according to OECD Test Guideline 422 in Sprague Dawley rats were conducted with sodium methanethiolate (see Table 1).

Tab. 1 Studies of repeated toxicity after oral administration of sodium methanethiolate

Species, strain, number per group	Exposure	Findings	References
rat, Sprague Dawley, 3 ♂, 3 ♀	14 days, 0, 5, 15, 45 mg/kg body weight and day in water, 7 days/week, gavage, range-finding	45 mg/kg body weight: NOAEL, increased salivation (not evaluated as adverse), no effects on body weights, food intake, no gross-pathological damage	OECD 2008
rat, Sprague Dawley, 6 ♂, 6 ♀	14 days, 0, 60, 75 mg/kg body weight and day in water, 7 days/week, gavage, range-finding	60 mg/kg body weight: ♂, ♀: hypoactivity, increased salivation, absolute and relative spleen weights ↑; ♀: exhaustion, lateral position; ♂: food intake ↓, 1 ♂ died (necropsy: foamy reddish contents in trachea and lungs); 75 mg/kg body weight: ♂, ♀: hypoactivity, sedation, lateral position, increased salivation and lacrimation, dyspnoea, body weight gains ↓, absolute and relative spleen weights ↑, enlarged spleen (2 ♂, 1 ♀); ♂: food intake ↓; ♀: spasms, exhaustion; 1 ♀ died (necropsy: dilated lungs, foamy contents in lungs)	OECD 2008
rat, Sprague Dawley, 10 ♂, 10 ♀	8–9 weeks, 0, 5, 15, 45 mg/kg body weight and day in water, 7 days/week, gavage, OECD Test Guideline 422	15 mg/kg body weight: NOAEL; 45 mg/kg body weight: ♂, ♀: hypotonia, ataxia, increased salivation, absolute and relative spleen weights ↑, haemoglobin concentration ↓, incidences of extramedullary haematopoiesis and severity of haemosiderosis in the spleen ↑, green pigment in a number of Kupffer cells; ♂: body weight gains ↓ (week 1), MCV ↓, sinusoidal ectasia; ♀: MCHC ↓, erythrocyte count ↓, haematocrit ↓, extramedullary haematopoiesis in liver ↑ no changes in FOB	Arkema Inc and Chevron Philips Chemical Company LP 2005

FOB: functional observational battery; MCHC: mean corpuscular haemoglobin concentration; MCV: mean corpuscular volume

In the first range-finding study, 3 animals per group were treated with 0, 5, 15 or 45 mg sodium methanethiolate/kg body weight per day by gavage. In the high dose group increased salivation was observed; no other treatment-related effects were found. In the second range-finding study with 6 animals per group, sodium methanethiolate doses of 0, 60 or 75 mg/kg body weight and day were used. Treatment-related clinical signs, mortality, retarded body weight gains and increased absolute and relative spleen weights occurred in both dose groups (OECD 2008).

In the screening study carried out according to OECD Test Guideline 422, 10 male and 10 female rats per group were given gavage doses of 0, 5, 15 or 45 mg sodium methanethiolate/kg body weight and day on 7 days a week. Treatment began 28 days before mating and lasted 8 weeks in the males, and between 8 and 9 weeks in the females up to day 4 after birth. Only in the high dose group were effects observed in the parent animals: in both sexes, in addition to some clinical signs, retarded body weight gains, reduced feed intake and changes in haematological parameters were seen (see Table 1). Absolute and relative spleen weights were increased; extramedullary haematopoiesis and haemosiderosis increased in incidence and severity. The severity of extramedullary haematopoiesis was increased in the liver of the females; greenish pigment was noticed in some Kupffer cells. The NOAEL (no observed adverse effect level) in this study was 15 mg sodium methanethiolate/kg body weight and day (Arkema Inc and Chevron Philips Chemical Company LP 2005).

Local effects on skin and mucous membranes

Data for methyl mercaptan are not available. Studies with sodium methanethiolate of skin and eye irritation cannot be used for this end point because sodium methanethiolate is a strong alkali while methyl mercaptan is a weak acid.

Allergenic effects

In a maximization test in 10 female and 10 male Dunkin Hartley guinea pigs, intradermal and topical induction was performed with 1% preparations and challenge treatment with a 10% preparation of the test substance in physiological saline. However, it is not clear whether the concentration data refer to the active substance or to the 21.2% solution of sodium methanethiolate in water provided for testing. Prior to topical induction, a 10% preparation of sodium lauryl sulfate in petrolatum was applied non-occlusively. Readings taken 24 hours after the challenge revealed weak erythematous reactions (grade 1) in 6 of 10 males and 4 of 10 females, but not after a further 24 hours; the authors did not regard these as signs of sensitization. More pronounced erythematous or oedematous reactions (at least grade 2) did not occur at any time (Elf Atochem Rotterdam BV 1994). The results cannot be used for the evaluation due to unclear documentation and deviations from the test guideline.

Reproductive and developmental toxicity

Fertility

In the screening study in rats carried out according to OECD Test Guideline 422, which was already described in detail in the Section “Oral administration”, no effects on the reproduction parameters mating index, time to mating, fertility index, duration of pregnancy, pregnancy index, number of pups, live pup index, number of live pups, survival index on day 4 after birth, and sex ratio were found. Histopathological examination of the reproductive organs did not reveal any unusual, substance-related findings, nor were the number and morphology of the examined sperms affected. The NOAEL for toxic effects on fertility in this study was 45 mg/kg body weight and day, which was the highest dose tested. The NOAEL for parental toxicity was 15 mg/kg body weight and day (Arkema Inc and Chevron Philips Chemical Company LP 2005).

Developmental toxicity

In the screening study according to OECD Test Guideline 422, already described in detail in the Section “Oral administration”, no foetotoxicity and no externally visible effects on the development of the offspring were observed up to the highest tested, maternally toxic dose of 45 mg sodium methanethiolate/kg body weight and day (Arkema Inc and Chevron Philips Chemical Company LP 2005). Teratogenicity and skeletal variations were not investigated in this study.

Genotoxicity

In vitro

No studies are available for methyl mercaptan.

In the Salmonella mutagenicity test, sodium methanethiolate was tested at concentrations of between 0 and 5000 µg/plate in the strains TA98, TA100, TA102, TA1535 and TA1537 in both the absence and presence of a metabolic activation system. Cytotoxicity occurred at 1000 µg/plate and above and at 2500 µg/plate and above, respectively. Sodium methanethiolate was not mutagenic in either the plate incorporation or pre-incubation tests (Elf Atochem Industrial Chemical BV 1992).

In human lymphocytes, concentrations between 30 and 480 µg sodium methanethiolate/ml (21% aqueous solution) were tested for the induction of chromosomal aberrations. Without metabolic activation the cells were treated for 20 or 44 hours, in the presence of a metabolic activation system the treatment duration was 3 hours with a 20-hour or 44-hour incubation period after treatment. Structural chromosomal aberrations were not induced. Without the addition of a metabolic activation system, there was an increase in the number of polyploid cells after 44 hours of treatment (0%, 4% and 14.5% in the controls, and 90 and 120 µg/ml groups, respectively). A second test with 50, 100

and 150 µg/ml and treatment for 44 hours resulted in a reduction of the mitosis index at the high concentration by more than 90% compared with the control value, and at 100 µg/ml led to an increase in polyploid cells to 3% with only a 14% reduction of the mitosis index. No effects were observed at 50 µg/ml (Elf Atochem S.A. 1995). The study does not provide information as to whether a pH control was performed. A commercial 21% aqueous sodium methanethiolate solution has a pH of > 10.

In vivo

A micronucleus test with bone marrow from Swiss Webster mice exposed to methyl mercaptan concentrations of 0, 114, 258 or 512 ml/m³ yielded negative results (Greim 2003).

Also with sodium methanethiolate no micronuclei were induced in the bone marrow of the treated Swiss OF1 mice after oral administration of 0, 12.5, 25 or 50 mg/kg body weight and day, twice at an interval of 24 hours (Elf Atochem Rotterdam BV 1999).

Summary

For **methyl mercaptan**, there is to date only one micronucleus test after inhalation exposure of mice available, which yielded negative results. **Sodium methanethiolate** is not mutagenic in bacteria. The substance does not induce structural chromosomal aberrations in human lymphocytes, but it does induce an increase in the number of polyploid cells, possibly due to a shift in pH. A micronucleus test in the bone marrow of mice after oral administration likewise yielded negative results.

Manifesto (MAK value/classification)

Critical effects are the effects on haematological parameters and on the central nervous system, and possibly also irritation of the mucous membranes. The odour nuisance is likely to be the main effect, but there is no reliable information as to the concentration at which excessive nuisance occurs. Concentrations between 0.0005 and 0.082 mg/m³ were given as the perception threshold for humans (Greim 2003).

MAK value. The behavioural change in the rats in the 90-day inhalation study, the huddling of the animals towards the periphery of the exposure chamber with upturned noses, which was already observed at the low concentration of 2 ml/m³ and which increased with increasing concentration, is probably due to the unpleasant odour or the irritant effect. In rats given 2 ml/m³, this behaviour was described as only “suggestive”. This change in behaviour continues to serve as the basis for the derivation of the limit value, but it is now interpreted as the result of an irritant effect or the unpleasant odour, which depends mainly on the concentration. As no new data for methyl mercaptan are available, the MAK value of 0.5 ml/m³ has been retained.

In a screening study carried out according to OECD Test Guideline 422 in rats with **sodium methanethiolate**, a NOAEL of 15 mg/kg body weight and day for systemic effects was obtained after 8 to 9 weeks of daily oral treatment. The following toxicokinetic data are taken into consideration for the extrapolation of this NOAEL to a concentration in workplace air: the daily exposure of the animals in comparison with the 5 days per week exposure at the workplace (7 : 5), the species-specific correction value for the rat (1 : 4), a possible increase in the effects with increasing exposure duration (1 : 4 because the exposure duration was between subacute and subchronic), the assumed oral absorption (100%), the body weight (70 kg) and respiratory volume (10 m³) of the person, and the assumed 100% absorption by inhalation. The concentration calculated from this is 9.2 mg/m³. As this value is derived from a NOAEL from experimental studies with animals, a concentration of 4.6 mg sodium methanethiolate/m³ (equivalent to 1.6 ml methyl mercaptan/m³) for the inhalable fraction would be obtained according to the procedures of the Commission (see Section I of the List of MAK and BAT Values, without applying the preferred value approach). Thus, the MAK value of 0.5 ml methyl mercaptan/m³ also protects against the systemic effects of methyl mercaptan, which is formed in the body from sodium methanethiolate.

Whether methyl mercaptan is irritating to the mucous membranes is unclear. The cases of poisoning observed in humans (Allied Chemical Corporation 1978; Greim 2003) do not indicate that irritation has a strong warning effect.

In a poorly documented study from Russia, it is reported that daily 3-hour exposure (for 5 or 10 days) of volunteers (5 days: n = 2; 10 days: n = 1) to the structurally similar **ethanethiol** at 3.9 ml/m³ led to adverse effects such as irritation, nausea and changes in the sense of taste, but not at 0.39 ml/m³ (Blinova 1965; Greim 2005). Similar effects can be assumed for methyl mercaptan.

Despite the uncertainties in the evaluation, the MAK value of 0.5 ml/m³ has therefore been retained.

Peak limitation. The change in the behaviour of rats exposed to 2 ml methyl mercaptan/m³ in a 90-day inhalation study is interpreted as a consequence of the unpleasant odour or irritant effect. Therefore, the substance is now assigned to Peak Limitation Category I. Since no data are available for humans, the excursion factor is 1.

Prenatal toxicity. In a screening study carried out according to OECD Test Guideline 422 with oral administration of sodium methanethiolate, no foetotoxic effects were observed up to the highest concentration tested of 45 mg/kg body weight and day despite maternal toxicity. Teratogenicity and skeletal variations were not examined in this study, so there are still no data available which would allow the assessment of the developmental toxicity of methyl mercaptan. The substance therefore remains classified in Pregnancy Risk Group D.

Germ cell mutagenicity. There are no new studies with methyl mercaptan. Some genotoxicity studies have been carried out with sodium methanethiolate and these are taken into account in the evaluation.

There are no studies of germ cells for either substance. Sodium methanethiolate is not mutagenic in bacteria. It does not induce structural aberrations in human lymphocytes but it does induce an increase in polyploid cells. Both sodium methanethiolate and methyl mercaptan do not induce micronuclei in mice after oral or inhalation exposure. The polyploidy effect in vitro may be due to a pH shift, since a 21% aqueous sodium methanethiolate solution has a pH of > 10.

Therefore, no data are available, including the studies with sodium methanethiolate, which would support the classification of methyl mercaptan in one of the categories for germ cell mutagens.

Absorption through the skin. From the NOAEL from an animal experiment, a systemically tolerable concentration of 1.6 ml methyl mercaptan/m³ (3.2 mg/m³) in the workplace air can be derived (see above). Assuming complete pulmonary absorption and a respiratory volume of 10 m³, the intake of 32 mg methyl mercaptan per work shift can be expected. The estimated amount absorbed dermally from the gaseous phase is only 0.03 mg, so that methyl mercaptan is not designated with an “H” (for substances which can be absorbed through the skin in toxicologically relevant amounts).

Sensitization. There are no findings of skin sensitization caused by methyl mercaptan in humans. Due to unclear documentation and deviations from the test guideline, a maximization test in guinea pigs with sodium methanethiolate cannot be used for the evaluation. There are no cases of respiratory sensitization. Methyl mercaptan is therefore not designated with either “Sh” or “Sa” (for substances which cause sensitization of the skin or of the airways).

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