Workplace Exposure Standard (WES) review

SULPHURIC ACID
(CAS NO: 7664-93-9)

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New Zealand Government

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1.0
Introduction

This WorkSafe New Zealand (WorkSafe) review considers whether the Workplace Exposure Standard (**WES**) for sulphuric acid should be changed.

It should be noted that all references to sulphuric acid in this document, unless otherwise stated, refer to sulphuric acid in a mist/aerosol.

This review considers the potential for exposures to sulphuric acid in New Zealand workplaces, the health effects and risks, exposure standards in other jurisdictions around the world, and the practicability of measuring sulphuric acid exposures given currently available analytical methods.

The review includes a recommendation to change the WorkSafe WES which is currently set at a **WES-TWA** of 1 mg/m^3, as published in the Special Guide *Workplace Exposure Standards and Biological Exposure Indices*, 9th Ed., (WorkSafe New Zealand, 2017).

In New Zealand, sulphuric acid carries a 6.7A notation for carcinogenicity. This means it is a known or presumed human carcinogen – the substance is either carcinogenic to humans, or the data indicate sufficient evidence in animal studies to demonstrate a causal relationship between exposure and the development of cancer, or an increase in tumours.

Terms that are **bold** (first occurrence only) are further defined in the Glossary.

Concentrations have been converted to **ppm** from **mg/m^3** (using the conversion factor in Table 1) unless the latter is specified as an occupational exposure standard.

Synonyms: Hydrogen sulphate, Matting acid, Oil of vitriol, Sulfuric acid, Vitriol brown oil.

2.0 Physical and chemical properties

Sulphuric acid is a dense oily, colourless, odourless liquid with a brownish hue when impure.

Chemical and physical properties of sulphuric acid include:

Molecular weight	98.08
Specific gravity	1.84 at 20°C (liquid)
Formula	H_2SO_4
Boiling point	338°C (98% pure)
Vapour pressure	<0.001 torr at 20°C
Vapour density	3.4 (air = 1)
Solubility	Soluble in all proportions of water or ethanol.
Conversion factors	1 ppm = 4.01 mg/m^3; 1 mg/m^3 = 0.25 ppm at 25°C and 760 torr
Reactivity	Can react violently with water or alcohol generating heat.
HSNO classification for >10% aqueous solution (NZ EPA, 2017)	6.1D (All), 6.1E (O), 6.7A, 6.9A (All), 8.1A, 8.2B, 8.3A, 9.1C (C), 9.1 (All)

TABLE 1: Chemical and physical properties of sulphuric acid

3.0
Uses

Sulphuric acid is very widely used in chemical manufacture and industrial processes.

This includes for batteries, detergents, fertilizers, explosives, pharmaceuticals, petroleum, steel paper products, textiles, metal cleaning, electroplating, food processing, jewellery manufacturing, leather and printing industries (HSDB, 2016).

The number of workers potentially exposed in New Zealand is estimated as 19,830 (Statistics New Zealand data for 2015). Occupational exposure to sulphuric acid is predominantly as a mist but dermal contact with the liquid is also a potential route of exposure.

4.0 Health effects of sulphuric acid

IN THIS SECTION:

The health effects of sulphuric acid have been investigated.

Health effects of sulphuric acid mist have been extensively reviewed by, among others, the International Agency for Research on Cancer (**IARC**, 2012), the United States Department of Health and Human Services, the United States Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (**ATSDR**, 1998) and the European Scientific Committee on Occupational Exposure Limits (**SCOEL**, 2007). These reviews assessed studies on occupational exposure as well as experimental animal data available at the time. An additional literature search was conducted in April 2017 for this review. Further consideration was given to the Australian Institute of Occupational Hygienists *Sulphuric Acid Mist* Position Paper (**AIOH**, 2015).

The reactivity of sulphuric acid particles to water is critical to its effects when inhaled and is influenced by aerosol size and humidity of the environment both externally and within the respiratory tract. Sulphuric acid particles are hygroscopic. Consequently, as the particles attract water molecules in the humid airways, the greater the droplet size becomes and the greater the deposition compared with inert particles (ATSDR, 1998). Deposition increases with the depth of penetration. As the small sulphuric acid particle penetrates deeper into the smaller pathways of the airways, the droplet grows and becomes too large to be exhaled back out through those same airways. Thus, particle size (measured as mass median aerodynamic diameter (MMAD)) becomes important in the depth of penetration. Consequently, breathing patterns can also affect depth of penetration (ASTDR, 1998). Larger droplets deposit in the nose with smaller droplets penetrating to the larynx, trachea and then bronchi.

4.1 Non-Cancer

Humans

Single aerosol exposure to sulphuric acid can result in ocular and respiratory tract irritation and dental blackening. Human volunteers exposed to 20 mg/m^3 exhibited intense coughing, lachrymation, and rhinorrhoea. Lower dosages elicited slight changes in lung function (at 2 mg/m^3 for 1 hour) or throat irritation /coughing (0.8 to 1 mg/m^3) with a no effect level of 0.5 mg/m^3 (it should be noted there were variations in subjects and experimental conditions). Studies have shown reduction in mucociliary clearance at 1 mg/m^3 and to a lesser degree at 0.3 mg/m^3 (SCOEL, 2007).

Data from epidemiological studies for repeat inhalation exposure in humans and animals is of limited value due to historical difficulties in measuring airborne sulphuric acid concentrations however reports have been published indicating effects of itching eyes, nasal irritation/discharge, sneezing, nose bleeds, throat irritation, dry nose and cough occurring at levels of 0.15 mg/m^3. Dental erosion and blackening are well documented in occupational exposure (SCOEL, 2007).

Concentrated sulphuric acid liquid is corrosive to the skin and eye (SCOEL, 2007).

Animals

Acute exposure in experimental animals causes corrosion or irritation of the skin, eye and upper respiratory tract. It is acutely toxic by inhalation as an aerosol mist – the most severe response is seen in guinea pigs which display pronounced bronchoconstriction and laryngospasm. This response is not seen in other rodent species (SCOEL, 2007).

Sub-lethal inhalation exposure in rabbits (1 mg/m^3 for 1 hour) caused slowed mucociliary clearance, mild inflammatory reaction in the lungs and increased polymorphonuclear counts in bronchoalveolar lavage fluid. Inhalation of 20 mg/m^3 for 4 hours (median mass aerodynamic diameter of 1 µm) in guinea pigs caused dyspnoea, partial atelectasis, loss of ciliated cells in the upper airways, desquamation, oedema, inflammatory infiltration in alveoli and bronchoconstriction (SCOEL, 2007).

Repeat exposure inhalation has been assessed in many experimental species with differing exposure conditions. Effects on mucociliary clearance and the influence of humidity have also been investigated. The larynx was the target organ in rats showing exposure-related changes of squamous epithelial metaplasia, with the severity increasing with dose (SCOEL, 2007).

Repeat inhalation exposure in rabbits to up to 0.25 mg/m^3 caused decreased mucociliary clearance, decreased airway diameter, increased secretory cell count and increased bronchial reactivity. However no histopathological changes indicative of respiratory tract irritation were observed (SCOEL, 2007).

A repeat dose inhalation study in primates indicated increasing toxicity with increased droplet size (SCOEL, 2007).

SCOEL summarise that:

> "Overall, no clear no observable adverse effects level (NOAEL) is discernable from the available repeated exposure studies in experimental animals, with evidence of various respiratory tract effects in rats, rabbits and monkeys on repeated exposure to concentrations in the range 0.125 – 0.38 mg/m^3" (SCOEL, 2007).

4.2 Cancer

Humans

Epidemiological studies reveal an increased risk of laryngeal cancer from occupational exposure to sulphuric acid mists. The presumed mechanism is by chronic inflammation of the epithelium in the larynx caused by the acidity of the sulphuric acid aerosol. This hypothesis links with the findings of the rat inhalation study (Kilgour et al, 2000, cited in SCOEL, 2007). A threshold would apply to this presumed carcinogenic mechanism (ie the dose at which the buffering capacity of epithelial cells is overwhelmed and a significant fall in cellular **pH** occurs) (SCOEL, 2007).

Occupational exposure to sulphuric acid mists also increases the incidence of lung cancer, covering a latency of 20 years (IARC, 2012).

The IARC concluded:

- There is sufficient evidence in humans for the carcinogenicity of mists from strong inorganic acids.
- Mists from strong inorganic acids cause cancer of the larynx.

- A positive association has been observed between exposure to mists from strong inorganic acids and cancer of the lung.
- While it is plausible that areas of localised low pH from inhalation of inorganic acid mists could damage DNA and increase cancer risks, the evidence supporting DNA-damage induction or any other mechanism as the cause of observed cancers due to the inorganic mists is weak.
- Mists from strong inorganic mists are carcinogenic (Group 1) (IARC, 2007).

SCOEL were of the opinion that there were some weaknesses in the cancer studies with potential confounders not being taken into account however it did consider there was adequate evidence to conclude that occupational exposure to sulphuric acid is associated with an increased risk of laryngeal cancer (SCOEL, 2007).

The New Zealand Environmental Protection Authority classifies sulphuric acid (>10% aqueous solution) as 6.7A – known or presumed human carcinogen (EPA, 2017).

There is no human genotoxicity data available for sulphuric acid (SCOEL, 2007).

Animals

Data in experimental animals investigating carcinogenic potential of sulphuric acid in mists are limited and of little value due to the reactive nature of the compound. One study in hamsters (exposure to 100 mg/m^3, 6 hours/day, 5 days/week for life) did not reveal any increase in respiratory tract tumours, suggesting that hamsters may be resistant to sulphuric acid respiratory tract toxicity (SCOEL, 2007).

Experimental investigation of genotoxicity is similarly confounded by the acidic nature of the concentrated compound, however, sulphuric acid appeared non-mutagenic in bacterial assays. Clastogenicity in mammalian cells have been reported but are considered most likely a consequence of acid-induced pH changes, a known cause of artefactual positive results. There are no *in vivo* data (SCOEL, 2007).

4.3 Absorption, distribution, metabolism and excretion

Animal studies following inhalation exposure show that the sulphur from sulphuric acid is rapidly absorbed from the lungs into the blood, with the resulting formation of sulphate. Sulphate is a normal constituent of blood and is excreted in urine (ATSDR, 1998).

Sulphuric acid aerosol toxicity is dependent on the hydrogen ion content of the aerosol causing pH change at the site of contact. The higher the concentration the greater the effect due to insufficient acid neutralising capacity at the point of contact. It is proposed effects are exerted by changing extracellular and intracellular pH; pH being critical in growth control and cell differentiation disruption of which may lead to adverse outcomes.

5.0 Exposure standards and guidance values in use around the world

IN THIS SECTION:

Table 2 below shows the sulphuric acid exposure standards from around the world.

This information is published by the Institute for Occupational Safety and Health of the German Social Accident Insurance (Institut fűr Arbeitsschultz der Deutschen Gesetzlichen Unfallversicherung, 2017) and available at http://limitvalue.ifa.dguv.de

JURISDICTION OR ADVISORY BODY	8-HOUR LIMIT VALUE (mg/m^3)	SHORT-TERM LIMIT VALUE (mg/m^3)
Australia	1	3
Austria	0.1 inhalable aerosol	0.2 inhalable aerosol
Belgium	1	3
Canada – Ontario	0.2 thoracic fraction	
Canada – Québec	1	3
Denmark	1	2
European Union	0.05 thoracic fraction	
Finland	0.05 thoracic fraction	0.1 thoracic fraction
France	0.05 thoracic fraction	3
Germany (AGS)	0.1 inhalable aerosol	0.1 inhalable aerosol
Germany (DFG)	0.1 inhalable aerosol	0.1 inhalable aerosol
Hungary	1	1
Ireland	0.05	
Israel	0.3	
Italy	0.05	
Japan	1	
Latvia	1	
New Zealand	1	
People's Republic of China	1	2
Poland	1	3
Singapore	1	3
South Korea	0.2	0.6
Spain	1	3
Sweden	0.1 inhalable aerosol	0.2
Switzerland	0.1 inhalable aerosol	0.1 inhalable aerosol
The Netherlands	0.05 thoracic aerosol	
Turkey	0.05	
USA – NIOSH	1	
USA – OSHA	1	
United Kingdom	0.05 thoracic aerosol	

TABLE 2:
Exposure standards for sulphuric acid from around the world

It is noted that the only organisations from whom we could get information as to how and why they set occupational exposures standards were **ACGIH®**, SCOEL and DFG.

5.1 New Zealand

WorkSafe's WES for sulphuric acid has been unchanged since adoption in 1994.

5.2 ACGIH®

The ACGIH® TLV-TWA is 0.2 mg/m³ measured as thoracic particulate fraction (ACGIH®, 2004). It is classified as an A2 suspected human carcinogen (when contained in strong inorganic acid mists). The principal considerations for determining this TLV® were:

- Data showing slight histologic and functional changes in the lungs of non-human primates at 0.5 to 2.4 mg/m³ following chronic exposure.
- Studies on animals and humans showing that acute exposure can alter trachea-bronchial clearance mechanisms
- A dose-response relationship shown between the exposure concentration of sulphuric acid and alteration in clearance. Low concentrations tended to increase clearance, whereas at higher concentrations tracheobronchial clearance was retarded
- Studies showing individuals with pre-existing respiratory disease, such as asthma, are more susceptible to sulphuric acid inhalation.
- It appears that most of the effects from exposure and the adverse effects on mucociliary clearance can be reduced and eliminated in many of the exposed persons if exposure is kept below 0.25 mg/m³.

The TLV-TWA of 0.2 mg/m³ is intended to minimise the potential for reductions in pulmonary function in individuals with pre-existing respiratory disease as well as minimising effects on mucociliary clearance.

As particle size of sulphuric acid mists is generally less than 10 µm, ACGIH® recommend applying the TLV-TWA to a thoracic value (using thoracic measurement methods) to protect against adverse effects on clearance and pulmonary function changes, as well as laryngeal cancer.

5.3 SCOEL

The SCOEL recommendation was an 8 hour WES-TWA of 0.05 mg/m³ (measured as inhalable fraction) and a **STEL** of 0.1 mg/m³. They acknowledge that it may be challenging to measure to these levels (SCOEL, 2007).

Their WES-TWA was determined after taking into account all available data but particularly the potential for carcinogenic affects and also experimental animal data showing slight respiratory tract changes in rats at 0.3 mg/m³ following repeat inhalation exposure with the possibility of health effects of significance occurring at 0.1 mg/m³.

5.4 DFG

The DFG 8 hour WES value for sulphuric acid is 0.1 mg/m³ (inhalable aerosol fraction), and a peak limit value is set at 0.2 mg/m³.

They considered the most sensitive endpoint in man is the alteration in mucociliary clearance, and therefore based the **MAK** value on human volunteer studies in which exposure to 0.3 mg/m³ or greater resulted in consistent effects on clearance of sulphuric acid. The DFG considers this to be a provisional value requiring more data from longer term human exposure, however the value is supported by experimental animal data.

Sulphuric acid is considered to be a category 4 carcinogen – substances that can cause cancer in humans or animals and for which a MAK (WES) can be derived, as the mechanism is non-genotoxic.

5.5 AIOH

The AIOH considered that although there are information gaps for health aspects of sulphuric acid mist, there was sufficient documentation to derive a WES (AIOH, 2015). They recommended a WES-TWA of 0.1 mg/m^3, and STEL of 0.5 mg/m^3. They reported:

- Measurement should be of the inhalable fraction.
- The STEL value is feasible to measure – but may not be particularly useful in its purpose of warning of possible acute effects as the results of monitoring will need to be analysed at a lab and thus are not available at the time of sampling.
- The measured exposure concentration can vary significantly depending on the sampling method chosen, and as such they recommend sampling method AS 3640 (for inhalable particulate).

In making their recommendation they reported studies that found:

- non-malignant respiratory effects exist at 1 to 3 mg/m^3
- short-term reduced lung clearance rates were observed at 0.1 mg/m^3
- 0.2 mg/m^3 can cause coughing or sneezing
- worker exposure to about 0.5 mg/m^3 has been reported to cause acute effect symptoms including sneezing, irritated nose, cough, runny nose and dry nose
- chronic effects were noted in rats exposed at 0.5 and 1.0 mg/m^3 but effects at 0.2 mg/m^3 were minimal
- a review of animal studies found effects in several species at exposure levels above 1 mg/m^3, while effects were not noted in monkeys exposed at 0.1 mg/m^3.

6.0 Analytical methods for the assessment of airborne sulphuric acid

A common practice in New Zealand to measure airborne sulphuric acid mist is using a modification of the NIOSH Method 7908 (2014).

Using this method a 15 to 2,000 litre air sample is collected onto a quartz fibre filter or **PTFE** membrane filter using a sampling train set at a flow rate of 1 to 5 litres of air per minute. Following exposure of the filter for an appropriate period of time, the filter is extracted with alkaline solution followed by analysis using ion chromatography with conductivity detection. The detection limit of this method has been quoted as 0.5 µg per sample for sulphuric acid.

This would allow a concentration of 0.0005 mg of sulphuric acid mist per m^3 of air to be quantified over a collection period of approximately 8 hours, at a flow rate of 2 litres of air per minute. The sampling time and/or flow rate can be adjusted within the guidelines of the method.

7.0
Discussion and recommendation

WorkSafe does not consider its current WES-TWA of 1 mg/m^3 ppm is acceptable given health effects are reported below this level.

It is proposed that WorkSafe New Zealand lower the WES-TWA to 0.1 mg/m^3, to minimise the potential for respiratory tract effects and laryngeal cancer. This value is in line with the most up to date review carried out by the AIOH in 2015.

Appendices

IN THIS SECTION:

Appendix 1: Glossary

TERM	MEANING
ACGIH®	The American Conference of Governmental Industrial Hygienists (ACGIH®) is a member-based organisation, established in 1938, that advances occupational and environmental health. Examples of this include their annual edition of the TLVs® and BEIs® book and work practice guides. Store at www.acgih.org/store
AIOH	Australian Institute of Occupational Hygienists.
ATSDR	Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.
DFG	Deutsche Forschungsgemeinschaft (German Research Foundation), the Permanent Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Federal Republic of Germany. The science-based MAK values are recommended to the German Minister of Labour and Social Affairs for possible adoption under the German Hazardous Substances Ordinance.
HSNO	Hazardous Substances and New Organisms Act, New Zealand.
IARC	The International Agency for Research on Cancer – an agency of the World Health Organisation, whose mission is to coordinate and conduct research on the causes of human cancer and to develop scientific strategies for cancer prevention and control.
MAK	Maximale Arbeitsplatz-Konzentration (trans. maximum workplace concentration). A German term.
mg/m^3	Milligrams of substance per cubic metre of air.
MMAD	Mass Median Aerodynamic Diameter.
NIOSH	The National Institute for Occupational Safety and Health (NIOSH) is the United States federal agency responsible for conducting research and making recommendations for the prevention of work-related injury and illness. NIOSH is part of the Centers for Disease Control and Prevention (CDC) within the U.S. Department of Health and Human Services.
NZ EPA	New Zealand Environmental Protection Authority
pH	The hydrogen potential – a measure of acidity.
ppm	Parts of vapour or gas per million parts of air.
PTFE	Polytetrafluoroethylene, or Teflon.
SCOEL	The Scientific Committee on Occupational Exposure Limits is a committee of the European Commission, established in 1995 to advise on occupational health limits for chemicals in the workplace within the framework of Directive 98/24/EC, the chemical agents directive, and Directive 90/394/EEC, the carcinogens at work directive.
TLV®	Threshold Limit Value (see TLV-TWA below). An ACGIH® term.
TLV-TWA	TLV® – Time-Weighted Average; the TWA concentration for a conventional 8-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed to, day after day, for a working lifetime without adverse effect. An ACGIH® term.
STEL (WES-STEL)	The 15-minute time weighted average exposure standard. Applies to any 15-minute period in the working day and is designed to protect the worker against adverse effects of irritation, chronic or irreversible tissue change, or narcosis that may increase the likelihood of accidents.
WES	Workplace Exposure Standard – WESs are values that refer to the airborne concentration of substances, at which it is believed that nearly all workers can be repeatedly exposed to, day after day, without coming to harm. The values are normally calculated on work schedules of five shifts of eight hours duration over a 40 hour week. A New Zealand term.
WES-TWA	The average airborne concentration of a substance calculated over an eight-hour working day. A New Zealand term.

Appendix 2: References

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