

REVIEW OF METHAM SODIUM, DAZOMET AND METHYLISOTHIOCYANATE (MITC) ATTACHMENT 2

Table 1 Identity of chemicals

Chemical	CAS No	Physical properties	Vapour pressure	Solubility	Other
Metham (a)	144-54-7 (metham) 137-42-8 (metham-sodium anhydrous) 6734-80-1 (metham-sodium dihydrate)	greenish-yellow liquid with a sulphide odour	not available (not considered to be volatile)	appreciably soluble in water	stable in aqueous solution but unstable when diluted. Subject to both hydrolysis and photolysis (b)
Dazomet (a)	533-74-4	white to off-white solid, with a weak intrinsic odour	1.4 kPa @ 20°C (low volatility)	solubility in water is low (0.3 g/100 g @ 20°C)	
MITC (a)	556-61-6	brown oily or clear yellow liquid, with a pungent horseradish-like smell	2.76 kPa @ 20°C (moderate volatility)	poorly soluble in water (8.2 g/L)	

a. In Schedule 6 of the Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP) (Australian Health Ministers' Advisory Council, 1995)

(b) Both processes yield mainly MITC. Other major products of hydrolysis are carbon disulfide and methylamine. Minor hydrolytic degradation products include elemental sulfur and 1,3-dimethylthiourea. Major products of photolysis are N-methylthioformamide, methylamine and elemental sulfur. Minor photolytic degradation products include N-methylformamide, carbon disulfide, carbon oxide sulfide and hydrogen sulfide (TGA, 1996)

Table 2: Toxicological end points obtained from animal studies relevant to short-term and long-term occupational exposure

Chemical	Worst acute oral toxicity (LD ₅₀) (mg/kg)	Worst acute dermal toxicity (LD ₅₀) (mg/kg)	Worst acute inhalation toxicity (LC ₅₀) (mg/m ³)	Eye irritation	Skin irritation	Skin sensitisation	No-Ob Effect (NOEL)
Metham (a)	450 (moderate: rat)	650 (moderate: rat)	>4700 (low: rat)	Moderate: rabbit (only 3% and 37% aqueous solutions)	TGAC ¹ - Corrosive (rabbit) 37% aqueous	Moderate to strong (guinea pigs)	10 mg (estak a rat develc study mater

				tested)	- severe irritant (rats and rabbits) 3% aqueous - slight irritant (rats and rabbits)		foetot and in devel study embry
Dazomet (b)	400 (moderate: rat, females)	>2000 (low: rat)	8400 (very low: rat)	Slight: rabbit (TGAC and EUP)	50% aqueous -slight irritant (rabbits) TGAC - not tested	Nil (guinea pigs)	> 1000 mg/kg (estak a 21 d derma for sy: toxicit
MITC (c)	72 (moderate: rat)	263 (moderate: rabbit)	540 (4 hour: moderate: rat)	TGAC - Corrosive: rabbit	TGAC - Severe: rabbit	Weak (guinea pigs)	30.7 n (10 pp (estak a 3 m inhala study clinica This d equiva 3.56 n bw/d kg wo

a. All registered metham-based EUPs are 50% in water. Hence, the acute toxicity profile of the products is expected to be similar to the TGAC.

1 - Technical grade active constituent

- b. It is envisaged that the TGAC and EUP for dazomet will have similar toxicity because the difference between the two forms is only one of particle size.
- c. No EUPs registered in Australia
- d. The NOELs used in the Risk Assessment
- e. Calculated assuming a minute volume of 29 L and a daily exposure of 4 hours (the duration of exposure in the rat inhalation study)

Table 4: Use pattern for metham

Use situation	Soil Injection	Rotary Tiller	Irrigation	Other

Seed beds, lawns and limited areas	25-50 L product in 50 L water per 1000 m ² (50% - 100% product and 25%-51% metham-sodium) Injection is followed by rolling and light watering or soil injection directly ahead of bed shaper.	1.1 L product in 12 L water per m ² (9% product and 5% metham-sodium) The solution is sprayed or sprinkled in front of the tiller, cultivated in, soil rolled over and watered.	-	Sprinkler can method - 60-100 mL product per 10 L water (0.6%-1% product and 0.3%-0.5% metham-sodium) ¹ The solution is sprinkled evenly over the prepared soil and soil watered immediately without run-off.
Field application (total area)	250-500 L product in 400-700 L water/ha (36% - 100% product and 18%-51% metham-sodium)	250-500 L product in 400-700 L water/ha (36% - 100% product and 18%-51% metham-sodium)	(a) Approved irrigation systems - trickle irrigation, linear or centre pivot systems ¹ - 600-800 L product per 900-1100 L water (55%-89% product and 27%-45% metham-sodium) (b) Flood irrigation - 610-790 L product/ha in a minimum of 15 cm water.	-
Field application (beds and rows)	250-500 L product in 400-700 L water/ha (36% - 100% product and 18%-51% metham-sodium)	250-500 L product in 400-700 L water/ha (36% - 100% product and 18%-51% metham-sodium)	Trickle irrigation - 250-800 L/ha (100% product and 51% metham-sodium). To be applied to beds previously prepared with trickle tape and plastic mulch.	Soil covering method - 400-800L product in 700-1000 L water (40%-100% product and 20%-51% metham-sodium). The solution is injected or dripped into moist soil directly ahead of the bed shaper, covered with 7-15 mm of soil and rolled immediately.

1. Some labels specifically indicate that these product may not be used through fixed, portable or solid set systems, travelling gun, boom or side roll systems, flood or any system using impact sprinklers, operating at high pressures or those causing drift.

Table 4, Cont: Use pattern for metham

Use situation	Soil Injection	Rotary Tiller	Irrigation	Other
PPotting soil		1.1 L product per 10-12 L water per 10 m ² (9%-11% product and 5%-6% metham-sodium)		(a) Loose mixed soil - 60-100 mL product per 10 L water over 2 m ² (0.65-1% product and 0.3%-0.5% metham-sodium). (b) Cement mixer - 600 mL per m ³ (51% metham-sodium). The undiluted product and soil are mixed within the cement mixer, then emptied into a pile and covered with water or plastic. (c) Shredder - 1.1 L product per 10-12 L water per 10 m ² (9%-11% product and 5%-6% metham-sodium). The diluted product is sprayed uniformly on the soil as it is ejected from the shredder.
Tobacco plant beds			Approved irrigation system - 9.75 L product in 700-900 L water per 100 m ² (1%-1.3% product and 0.5%-0.7% metham-sodium).	Spot treatment - 1.1 L product in 50 L water per 5 m ² (2.2% product and 1% metham-sodium).

Source: Metham product labels

Table 5: Airborne MITC and potential exposure incidents when applying metham using shank injection equipment

Replicate number (Rep), worker ID	Cab type	Eye and respiratory protective equipment	Inhalation exposure to MITC (mg/kg ai handled)	Inhalation exposure to MITC (mg/hr)	Potential exposure incidents
Rep 1: Worker B	closed cab with charcoal air filter	None	0.00187	0.301	Equipment maintenance
Rep 2: Worker B	closed cab with charcoal air filter	None	0.00240	0.494	
Rep 3: Worker B	closed cab with	Respirator and goggles	0.00932 (a)	1.97	Tractor problems: fumes experienced-

	cellulose air filter				relating to the filter and wind direction; respirator put on during replicate
Rep 4: Worker B	closed cab with cellulose air filter	Respirator and goggles	0.01220 (a)	3.12	
Rep 5: Worker B	closed cab with cellulose air filter	Respirator and goggles	0.0110	2.70	A lot of product was spilled when hose was connected to the spray tank and when hose was disconnected
Rep 6: Worker D	closed cab with cellulose air filter	Respirator and goggles	0.0110	2.70	
Rep 7: Worker D	Open cab tractor	Respirator and goggles	0.00346	0.774	
Rep 8: Worker D	Open cab tractor	Respirator and goggles	0.0458 (a)	6.71	Personal air sampler failure: equipment failure and replacement
Rep 9: Worker D	Open cab tractor	Respirator and goggles	0.0102	1.23	Worker turned on the spray before shanks were completely in the ground
Rep 10: Worker D	Open cab tractor	Respirator and goggles	0.00138	0.385	
Average (b)			0.0109	2.04	

Source - Rosenheck L (1993a) Worker Mixer/Loader and Applicator Exposure from Field Applications of Metham-Sodium, Pan-Ag Study No EF-91-360, August 1993, Sponsor Metham-Sodium Task Force c/o ICI Americas, Inc.

(a) CS₂ levels were above the MQL

(b) Arithmetic mean

Table 6: Airborne MITC and potential exposure incidents when applying metham using a sprinkler irrigation system

Replicate number (Rep), worker ID	Eye and respiratory protective equipment	Inhalation exposure to MITC (mg/kg ai handled)	Inhalation exposure to MITC (mg/hr)	Potential exposure incidents
Rep 1: Worker C	None	0.00243	0.286	The injection pump leaked for the last 1.5 hours it was operating
Rep 2: Worker E	None	0.00114	0.143	
Rep 3:	Respirator	0.00411	0.505	

Worker E	and goggles			
Rep 4: Worker E	Respirator and goggles	0.0241	2.95	Exposure to fumes caused by a change of wind direction requiring applicator to leave the field for 20 min. Worker experienced tearing of eyes when changing sprinkler lines and checking sprinkler heads, despite wearing goggles and respirator
Rep 5: Worker C	None	0.00938	1.17	Wind changed direction and blew metham fumes towards applicator
Rep 6: Worker C	Respirator and goggles	0.0242	3.02	Worker complained of strong fumes when he went into the field. Occasional change in wind direction caused watering of eyes
Rep 7: Worker C	Respirator and goggles	0.0404	4.96	Wind direction changed and strong fumes made worker leave the area
Rep 8: Worker E	Respirator and goggles	0.0386	4.82	Wind direction changed and strong fumes made worker leave the area
Rep 9: Worker E	Respirator and goggles	0.0268 (a)	3.32	Shifting winds caused the applicator to spend most of the replicate time away from the application zone
Rep 10: Worker E	Respirator and goggles	0.0365	4.79	Worker moved to the end of the field due to shifting winds. A possible inversion layer was noticed, application halted and water applied for approximately 0.5 hours. Metham application was resumed when odour dissipated. Worker replaced a shield that had fallen off an operating sprinkler.
Average (b)		0.0208	2.60	

Source - Rosenheck L (1993a) Worker Mixer/Loader and Applicator Exposure from Field Applications of Metham-Sodium, Pan-Ag Study No EF-91-360, August 1993, Sponsor Metham-Sodium Task Force c/o ICI Americas, Inc.

(a) CS₂ was >MQL (0.00016 mg/kg ai handled) (b) Arithmetic mean

Table 7: Airborne MITC residues and potential exposure incidents when applying metham using rotary tiller injection equipment

Replicate number (Rep), worker ID	Cab and filter type	Eye and respiratory protective equipment	Inhalation exposure to MITC (mg/kg ai handled)	Inhalation exposure to MITC (mg/hr)	Potential exposure incidents
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Rep 1: Worker D	Closed cab with charcoal air filter	Respirator	0.00557	1.15	Applicator left the cab to remove trash from blades and stood next to a dripping nozzle. He detected an odour in the cab and wore a respirator
Rep 2: Worker D	Closed cab with charcoal air filter	Respirator	0.0176	4.35	Odour detected in cab (no apparent cause)
Rep 3: Worker D	Closed cab with charcoal air filter	None	0.00333	0.939	Door of cab was open for unknown duration
Rep 4: Worker D	Closed cab with charcoal air filter	None	0.00257	0.634	
Rep 5: Worker D	Closed cab with charcoal air filter	None	0.00171	0.435	
Rep 6: Worker F	Closed cab with cellulose air filter	None	0.00294	0.818	
Rep 7: Worker F	Closed cab with cellulose air filter	None	0.00133	0.394	
Rep 8: Worker F	Closed cab with cellulose air filter	None	0.00672	1.79	Worker cleaned out spray tank filter at the end of the replicate
Rep 9: Worker F	Closed cab with cellulose air filter	None	0.00296	0.832	
Rep 10: Worker F	Closed cab with cellulose air filter	None	0.00797	2.13	
Geometric Mean (SD)			0.00393 (0.00460)	1.03 (1.13)	

Source: Rosenheck L (1993b) Worker Loader and Applicator Exposure from Field Applications of Metham-Sodium, Pan-Ag Study No 92205, May 1993 Sponsor Metham-Sodium Task Force c/o ZENECA Ag Products.

Table 8: Airborne MITC residues and potential exposure incidents when applying metham using center pivot sprinkler system

Replicate number (Rep), worker ID	Eye and respiratory protective equipment	Inhalation exposure to MITC (mg/kg ai handled) (a)	Inhalation exposure to MITC (mg/hr)	Potential exposure incidents
Rep 1: Worker E	None	0.000624	0.143	(b)
Rep 2: Worker E	None	0.000591	0.136	(b)
Rep 3: Worker B	None	0.000994	0.228	(b)
Rep 4: Worker B	None	0.000580	0.131	(b)
Rep 5: Worker B	None	0.000711	0.161	(b)
Geometric Mean (SD)		0.000685 (0.000154)	0.156 (0.036)	

Source: Rosenheck L (1993b) Worker Loader and Applicator Exposure from Field Applications of Metham-Sodium, Pan-Ag Study No 92205, May 1993 Sponsor Metham-Sodium Task Force c/o ZENECA Ag Products.

(a) all CS₂ residues below MQL (1m)

(b) No exposure incidents reported. No worker opted for goggles and/or respirator

Table 10: Exposure to airborne MITC and margins of exposure for workers handling metham by soil incorporation and chemigation techniques

Task	Situation	No of transfers (1)	MITC mg/hr (29 LPM)	MITC mg/m ³ (29 LPM)	MOE (2)	MITC mg/kg ai handled	MITC mg/kg bw/day	MOE (3)	C o h e
Loader	Rotary tillage (4)	one (5)	0.787	0.45	68	0.000323	0.008 (6)	445	V v r i a g n c o
	Injection/rotary (7)	one (5)	0.775	0.45	68	0.000282	0.006 (6)	593	V v r i a g n c o s e

	Fixed sprinkler (7)	four ⁽⁸⁾	1.50	0.86	36	0.00292	0.049 (9)	73	tr V v r i a g n c o s e t
	Centre pivot ⁽⁴⁾	six ⁽¹⁰⁾	0.354	0.20	154	0.0000560	0.002 (9)	1780	V v r i a g n c o
Applicator	Rotary tillage (4)		1.03	0.59	52	0.00393	0.100 (6)	36	O d t o c v c l f i v d r T w u c v c f i n r n c o
	Injection/rotary (7)		2.04	1.17	26	0.0109	0.231 (6)	15	F e i r v c f i v d r a

									g v t l c r a d c o v t l c r a d c o
	Fixed sprinkler (7)		2.60	1.49	21	0.0208	0.348 (9)	10	F e f p t r d a t: p b i r d a g F p v v r a g F e d o r a g V n o a
	Centre pivot (4)		0.156	0.09	341	0.000685	0.021 (9)	170	N o v r

(approx. 300 m)			
At point of application - 24 hours post-application	0.07	0.011	324
Study 2	<0.05	<0.008	>445
Operator breathing zone exposure			
Operator breathing zone exposure	<0.08	<0.013	>274
Operator breathing zone exposure	0.17	0.028	127
At point of application - 30 mins post application (e)	7.7 (d)	1.283	3
At point of application - 90 mins post application (e)	3.9 (d)	0.650	5
At point of application - 180 mins post application (f)	20.2 (d)	3.366	1
At point of application - 270 mins post application (f)	13.2 (d)	2.200	2
At point of application - 360 mins post application (f)	2.6 (d)	0.433	8
At point of application - 24 hours post-application (f)	<0.03	0.005	712

Source: Sheers R (1994) Melbourne Water - Sanafoam Vaporooter Trial, 7 November 1994 and Sheers R (1995) Melbourne Water - Sanafoam Vaporooter Trial, 13-14 February 1995, ICI Australia Operations Pty Ltd.

- a. Assumes a breathing rate of 10 m³ per working day; average body weight of 60 kg
- b. MOE based on the human dose (3.56 mg/kg bw/day) equivalent to the NOEL derived from a three month rat inhalation study using MITC (30.7 mg/m³) for a 60 kg worker
- c. Sampling time 65 minutes, corresponding to the time the Vaporooter was being pumped
- d. Values exceed the eye irritation threshold in cats of 0.2 mg/m³
- e. Manhole cover left completely open
- f. Manhole cover open approximately 2 cm