

Comments on Measurability of Specific SWA Proposed WESs

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Prepared by AIOH Workplace Exposure Assessment Committee

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1. Calcium Hydroxide

The AIOH had previously written:

“TWA value of 5 mg/m³ reduced to 1 mg/m³ and with addition of a STEL of 4 mg/m³, based on SCOEL (2008)¹ recommendation to protect against “sensory irritation”. This is like the UK HSE (and SCOEL) recommendation of a TWA value of 1 mg/m³ and a STEL of 4 mg/m³, both as the respirable fraction. The SWA documentation does not specify the size fraction to be monitored.

As noted by the SCOEL (2007) documentation, the “effects of CaO and Ca(OH)₂ are considered to be limited to the external surfaces of the body and no systemic effect is foreseen”. The AIOH commented to SWA that ‘Being an irritant only, should we even consider assigning a WES?’ Controls should be implemented if symptoms occur.

SWA state that “There is uncertainty regarding quantification of the recommended value with available sampling and/or analysis techniques.”

There can be difficulties in measuring calcium hydroxide concentrations in air as exposures in the workplace are often due to mixed levels from production of raw materials (e.g. clay, limestone and quartz) and cement dust. However, SCOEL (2008) state that, considering European Standard EN 482:2005, “there are no problems to measuring the long and the short-term exposures with OELs as TWA (8h)= 1 mg/m³ and STEL (15 min)= 4 mg/m³ respectively”. [OSHA Method ID-121](#) has a limit of detection of 0.0002 mg/m³.”

SWA ask “Are AIOH aware of a validated method and the LoQ?”

[TestSafe Australia](#) has a method for calcium hydroxide called alkaline dust, which is based on NIOSH Method 7401 (Issue 2). The LoQ is said to be 0.03 mg on the filter. However, it appears that TestSafe no longer offer the alkaline dust analysis. In fact, Method 7401 is no longer available in the [NIOSH Manual of Analytical Methods \(NMAM\) 5th Edition](#). However there are Methods 7302 and 7304, both titled ‘ELEMENTS by ICP (Microwave Digestion)’. The LoD for method 7302 was 0.002 mg on the filter while for Method 7304 the LoQ appears to be higher – around 0.1 mg on the filter.

Given these analytical limit values, we believe that you could successfully analyse for calcium with respect to the proposed WES as long as there are no other calcium-containing compounds present. However, we do not know of a validated method specifically for calcium hydroxide. We suggest you may need to analyse it along the same lines as that for calcium sulfate.

¹ SCOEL (2008). *Recommendation from the Scientific Committee on Occupational Exposure Limits for Calcium oxide (CaO) and calcium hydroxide (Ca(OH)₂*. SCOEL/SUM/137.

2. Copper, fume, dust & mist (as Cu)

SWA recommends that the TWA-WES for copper fume of 0.2 mg/m³ and for copper dusts and mists of 1 mg/m³ be each reduced to 0.01 mg/m³. This revised TWA-WES value is recommended to protect for irritant and adverse lung effects in exposed workers and is consistent with the SCOEL (2014) recommendation. SCOEL (2014) recommend a 0.01 mg/m³ exposure limit for the respirable fraction of copper, essentially the fume component, noting that it applies to copper and all its inorganic compounds.

SWA notes that there is uncertainty regarding quantification of the recommended value with currently available sampling and/or analysis techniques.

The AIOH have already submitted the following:

“Preferable that there are separate WESs for copper fume (0.05 mg/m³ respirable fraction) and copper dust and mist (0.1 mg/m³ inhalable fraction), as per an old ACGIH notification of change. Quantification of recommended values using currently available sampling and analysis techniques needs to be checked. A recent publication by Brand *et al* (2020) ‘[No Observed Effect Level \(NOEL\) for Systemic Inflammation by Copper and Zinc in Welding Fumes](#)’ suggests a NOEL for copper to be between 0.2 and 0.3 mg/m³.”

The SCOEL (2014) recommendation used the Gleason (1968) reference for determining repeated dose toxicity from human studies. They note that:

“The effects (general feeling of discomfort, slight sensations of chills and warmth, stuffiness of the head) were first reported some weeks after the start of exposure. Measured exposure was 0.12 mg/m³ but, according to the author, the workers may sometimes have been exposed to 2- to 3-fold higher concentrations. The effects did not disappear until an exhaust system was installed, which reduced exposure to 0.008 mg/m³.”

It should also be noted that a more recent publication, ‘[A Health Surveillance Study of Workers employed at a Copper Smelter – Effects of Long-Term Exposure to Copper on Lung Function using Spirometric Data](#)’, by Haase *et al* (2021), concluded that:

“.... cumulative inhalable copper dust exposure averaging 4.61 mg/m³-years over an exposure duration of ~22 years is not associated with adverse effects on lung function. Cumulative inhalable copper exposure of 4.61 mg/m³-years roughly equates to a respirable copper concentration of 1.06 mg/m³-years (range of 0.32 to 1.80 mg/m³-years). Under the proposed SCOEL, respectively MAK value of 0.01 mg/m³ as respirable fraction, a worker would need to be exposed for more than 1,000 years to achieve the mean cumulative exposure of the assessed cohort. The absence of an adverse effect on lung function, even among workers in the highest cumulative exposure tertile, supports the conclusion that at the observed exposure levels, copper has not had measurable impact on FEV₁, FVC and FEV₁/FVC.”

In addition, only Germany and New Zealand has as yet adopted the SCOEL recommended 0.01 mg/m³ limit value. The Haase *et al* (2021) publication suggests that such a limit is too low.

SWA ask “Can you confirm that for Copper, fume, dust and mists (as Cu) a TWA of 0.01 mg/m³ can be accurately measured using currently available sampling and analysis techniques?”

We suggested that SWA adopt the values proposed by the ACGIH on an interim basis, as above. More review is required.

Copper dust and fume can be measured on a filter by XRF to a LoQ of 1 µg on the filter at TestSafe Australia. An even lower LoQ could be achieved with ICP-MS. The RQL for copper as stated in the [OSHA Sampling and Analytical Method](#) number 1006 is 0.0003 mg/m³. For Method number 7029, it is around 0.05 mg/m³, while for [NIOSH Analytical Method](#) number 7303 it is around 0.001 mg/m³. Hence, yes it can be accurately measured using currently available sampling and analysis techniques.

3. Acrolein

SWA recommends that the TWA-WES for acrolein of 0.1 ppm and the STEL of 0.3 ppm be reduced to 0.02 and 0.05 ppm, respectively. This is to protect for irritation of the eyes, the mucous membrane and skin of exposed workers.

SWA state that these recommended values are below the current limit of detection for available sampling and analysis techniques.

The AIOH have already submitted the following:

“SWA Recommended WES of 0.05 mg/m³ is at or below NIOSH 2501 LoD of 2ug; under the OSHA Method 52 Quantitation limit of 6.1 ug/m³ (as noted in the WES draft evaluation report). When assessing whether or not accurate sampling and analytical methods are available to measure exposure to compare with or assess compliance against a recommended exposure standard, the European Commission (2017) state that “Measurement techniques should be able to assess exposure at: 0.1 times the OEL for 8-hour TWA”.

SWA ask “Can AIOH clarify why the WES would be considered “around the LoQ” and not readily quantifiable?”

TestSafe Australia uses a modification of OSHA Method 64 for acrolein and has an LoQ of 0.25 mg on the filter. Leeder Analytical in Melbourne quotes an LoD of 2 ng acrolein using thermal desorption tubes and analysis by GC-MS-MS. That’s an approximate LoQ of 0.2 µg/m³ (about 0.08 ppm) for a 10 L sample. So, it would not be possible to quantitate exposure at the STEL and difficult to quantitate the TWA WES.

Note our reference to the prerequisite that measurement techniques should be able to assess exposure at 0.1 times the OEL for an 8-hour TWA. The reasoning is as explained in our joint AIOH / NATA paper on measurement of respirable crystalline silica.

4. Calcium Sulfate

SWA recommends that the TWA-WES for calcium sulfate of 10 mg/m³ be reduced to 1.5 mg/m³ (presumably as the respirable fraction!). This is to protect for local effects in the lungs of exposed workers.

SWA notes that there is uncertainty regarding quantification of the recommended value with currently available sampling and/or analysis techniques.

The AIOH have already submitted the following:

“A UK HSE 2003 review determined there was limited documentation on the basis of the limit was uncertain for this substance but retained their WEL. Being an irritant only, should we even consider assigning a WES?”

SWA ask “Can you confirm that for Calcium sulfate a TWA of 1.5 mg/m³ can be accurately measured using currently available sampling and analysis techniques?”

NIOSH Method 7020 can measure calcium and compounds (as Ca) in the range 1 to 20 mg/m³ for an 85 L air sample. This is an elemental analysis, not compound specific. Given that measurement techniques should be able to assess exposure at 0.1 times the OEL for an 8-hour TWA, this method may not have an adequate LoQ. OSHA has a partially validated method (PV2121) for calcium sulfate with reliable quantitation limit of 0.066 mg. Samples collected for this method are first analysed gravimetrically. If the gravimetric result of a sample yields a concentration below the OEL, it will be reported as the calculated air concentration for the requested compound solely from the gravimetric result, qualified as less than or equal to the gravimetric result. If over the OEL, the sample will proceed for elemental analysis.

The AIOH concur that this analysis would probably be done gravimetrically in most cases rather than specifically analysing for CaSO₄ or even for Ca. The gravimetric LoQ is between about 0.02 and 0.1 mg/m³ depending on whether a 5 or 6 figure microbalance is used for the gravimetric analysis. So, quantitation at the WES is not an issue.

For further communication please contact the AIOH.

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