

# Influence of the experimental conditions on manganese bioaccessibility and oxidative potential of welding fumes

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Welding Fumes (WF) were classified in 2018, as group 1 carcinogens for human lungs by the International Agency for Research on Cancer. WF are mainly composed of ultrafine particles (UFP) of metal oxides. Excessive inhalation of manganese (Mn) from WF can lead to several adverse health effects as neurodegenerative disease and lungs damage (Antonini et al., 2006).

Mn is known to catalyze the reactive oxygen species (ROS) production. ROS can react quickly with lung fluids and epithelial cells causing their damage (Newby et al., 2015). A previous study showed that Mn and Cu were the most soluble metals in phosphate buffer (PB) and the main contributors to OP in WF extracts (Ghanem et al., 2021). To estimate the potential health effects on exposed workers, analysis may be carried out to assess the contribution of Mn bioaccessibility on the oxidative potential (OP) of WF-UFP.

Experimental conditions such as extraction duration and solution, and storage duration before analysis of WF are essential parameters in the assessment of the bioaccessibility of Mn and the OP WF-UFP. Therefore, in this work we generated stainless steel WF using an automated generation bench and collected on 37-mm PVC filters. An elementary mapping at the particle scale were performed using a Scanning Transmission Electron Microscopy (STEM). WF total metal composition was determined after a total acid digestion followed by an analysis using ICP-MS. Mn bioaccessibility (ratio of soluble Mn) was studied under physiological conditions (pH 7.4 and 37°C) in a phosphate buffer (PB) solution (Ghanem et al., 2021) and in an artificial lung lining fluid, Hatch's solution (Berlinger et al., 2008). In addition, the oxidative potential (OP<sup>DTT</sup>) of UFP-WF was evaluated by following the dithiothreitol (DTT) consumption rate (in  $\mu\text{mol DTT L}^{-1} \text{min}^{-1} \text{mg}^{-1}$ ), using a UV-Vis microplate reader at 412 nm (Spark<sup>TM</sup> 10M).

Our results showed that WF stainless steel was composed of about 30% Mn oxides. STEM mapping showed that Mn disperses along the WF particles in a heterogeneous way. Similar bioaccessibility of Mn was found in phosphate buffer ( $27\% \pm 2\%$ ) and in Hatch's solution ( $26\% \pm 3\%$ ) showing that there is no apparent effect of the nature of the solution on Mn bioaccessibility. This can be linked to a complexation with species present in both the Hatch solution and the

phosphate buffer such as phosphates to form  $\text{MnHPO}_4$  as suggested by the Visual MINTEQ<sup>®</sup> software or to a localization rather on the surface of the particles, in connection with its relatively low boiling point (1962°C). OP<sup>DTT</sup> rates were higher for UFP-WF samples after 0.5 h extraction in PB than after 24 h while Mn bioaccessibility increases from  $22.5 \pm 1.3 \text{ mg g}^{-1}$  (0.5h) to  $37.5 \pm 0.8 \text{ mg g}^{-1}$  (24h). This can be explained by potential precipitation of Mn over time (Reed et al., 2021).

The increase of the storage duration of WF-UFP in the air from 0.5 h to 35 days showed a significant decrease in Mn bioaccessibility and the measured OP<sup>DTT</sup> (Table 1). This effect may be explained by variation of the Mn speciation in contact with  $\text{O}_{2(g)}$  during the storage period. This also suggests that other factors including the loss of short-live ROS that might influence the OP<sup>DTT</sup>.

**Table 1. Mn Bioaccessibility and OP<sup>DTT</sup> of WF-UFP PB extracts following different storage durations.**

Storage durations	Mn Bioaccessibility ( $\text{mg g}^{-1}$ )	OP <sup>DTT</sup> ( $\mu\text{mol DTT L}^{-1} \text{min}^{-1} \text{mg}^{-1}$ )
0,5 h	$12.4 \pm 1.7$ (n=8)	$0.45 \pm 0.03$ (n=8)
1 day	$11.6 \pm 1.3$ (n=6)*	$0.39 \pm 0.02$ (n=6)*
7 days	$9.4 \pm 0.8$ (n=6)*	$0.39 \pm 0.03$ (n=4)*
35 days	$9.1 \pm 0.8$ (n=4)*	$0.35 \pm 0.02$ (n=4)*

\*results significantly different from Fresh

This work confirms that Mn is a key element to assess the toxicity of WF. There is a strong relationship between Mn bioaccessibility and OP<sup>DTT</sup> of UFP-WF. Further studies are needed for an advanced characterisation of specific evolution of Mn speciation and ROS evolution under different experimental conditions. OP<sup>DTT</sup> analysis using online method may an alternative to reduce the effect of storage duration.

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