# Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

# Experimental factors influencing the bioaccessibility and the oxidative potential of transition metals from welding fumes<sup>†</sup>

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#### S1. Welding fumes generation bench

The welding bench uses the MIG/MAG process (SAF-FRO; Air Liquide) with M21 shielding gas, consisting of 82% Ar and 18% CO<sub>2</sub>, in short-circuit mode (I  $\approx$  132 A, U  $\approx$  16.6 V). The quantification limits and uncertainties were calculated according to the standard NF ISO (15767)<sup>2</sup>.



Figure S1. Welding fume generation bench<sup>1</sup>.

## S2. Hatch's solution composition and preparation

The preparation protocol of the Hatch's solution is adapted from the studies of Berlinger et al.  $(2008)^3$ , Ellingsen et al.  $(2013)^4$  and Kastury et al.  $(2017)^5$ .

Add the inorganic compounds and D-glucose (D-(+)-Glucose) to a decontaminated 50 mL volumetric flask in the order listed (Table S2) to avoid any precipitation and then make up to volume with 50 mL of ultrapure water. Ultrapure water is added between each step to recover everything and wait for the complete dissolution of the compound before adding the next one. The initial pH of the Hatch's inorganic solution is adjusted to  $7.4 \pm 0.2$  by adding commercial HCl (1 mol L<sup>-1</sup>) or NaOH (1 mol L<sup>-1</sup>) solutions.

Weigh each of the antioxidants, proteins and lipids (antibacterial) in 3 different decontaminated 50 mL flasks as indicated in Table S2. Note that the DPPC is solubilized in an ultrasonic bath heated to 40°C. The 4 solutions (inorganic compounds, antioxidants, proteins and lipids) are then mixed in a 250 mL Teflon bottle. On the day of extraction, the final pH of the solution is

measured (pH after 12h of storage). An aliquot of the Hatch's solution is placed in an incubator at 37°C for 10 min and shaken continuously on a shaking table before starting the extraction.

Hatch's solution can be stored in a refrigerator  $(2 - 8^{\circ}C)$  for a few weeks after preparation. On the other hand, aliquots stored at 37°C or at room temperature can be used for a maximum of 2 to 3 days as the proteins can coagulate and prevent centrifugation of the entire Hatch's solution.

Table S2.1. Constituents of Hatch's solution. All chemicals disclosed by Sigma-Aldrich except calcium chloride (Supelco) and magnesium chloride (Merck).

Flask 50 mL	Order of addition	Chemical compound	Purity (%)	Mass (g) for 1 L	Mass (mg) for 0.2 L		
Vial 1		Inorganic salts					
	1	NaCl	99.99	7	1400		
	2	$CaCl_2.2H_2O$		0.2251	45.02		
	3	Na <sub>2</sub> HPO <sub>4</sub>	≥99	0.1196	23.92		
	4	NaHCO <sub>3</sub>	≥99.5	2.27	454		
	5	KH <sub>2</sub> PO <sub>4</sub>	≥99	0.03	6		
	6	KC1	99.5	0.37	74		
	7	MgCl <sub>2</sub> .6H <sub>2</sub> O		0.21	42		
	8	MgSO <sub>4</sub>	≥98	0.0342	6.84		
	9	D-glucose (D-(+)-Glucose)		1	200		
		Ajust pH to 7.4					
Vial 2		Organic compounds					
		Antioxidants					
	10	Ascorbic acid	99.7-100.5	0.05	10		
	11	Uric acid	99	0.025	5		
	12	Glutathione	≥98	0.05	10		
Vial 3		Protein					
	13	Serum albumin (bovine)	≥96	10	2000		
	14	Lysozyme		2.5	500		
	15	α- Tocopherol (vitamin E)		0.001	0.2		
	16	Apo- transferrin (bovine)		0.2	40		
Vial 4		Lipid					
	17	Phosphatidylcholine DPPC (	≥98	10	2000		
		egg)					
		Ultrasound bath at 40°C					
		Antibacterial/fungal					
	18	Benzalkonium chloride _ Or alkylbenzyldimethylamonium chloride _		0.05	10		

Table S2.2. Limit of detection (LOD) obtained for the main elements analyzed in methodological after 24h-extraction in Hatch's solution and phosphate buffer solution.

LOD (mg.g <sup>-1</sup> )	Cu	Cr	Fe	Mn	Ni
Hatch	0.6	0.1	1	5	0.4
Phosphate buffer	1.0	0.9	160	16	1.1

LOD is calculated as 3 x Standard Deviation of the average methodological blanks

## S3. Mass percentage of metal oxides in welding fumes

Table S3. Mass percentage of metal oxides constituting the certified reference material of stainless-steel welding fumes (CRM of SSWF-1) analyzed by Butler et al.  $(2014)^6$ ; and the welding fumes (WF) produced by the stainless-steel, wire and stainless-steel bars or mild-steel bars (n = 12) using the welding bench in this study.

Samples (%)	Oxide <sup>*</sup> (%)	CRM of SSWF-1	<b>Generated WF</b>	<b>Generated WF</b>
Welding wire		Stainless-steel	Stainless-steel	Stainless-steel
Welding bars		N/A	Stainless-steel	Mild-steel
	$Cr_2O_3$	24.5	33	32
	CuO	0.50	0.48	0.61
	Fe <sub>3</sub> O <sub>4</sub>	41	38	37
	MnO	29	16	17
	NiO	4.7	6.5	5.9
	ZnO	0.30	0.29	0.96
Other oxides	/	/	5.73	6.53

\*Metal oxides most likely to be present in WF - <sup>N/A</sup> Not analyzed



## S4. X-ray crystallography (XRD) results of welding fumes

Figure S4. XRD spectrum of fresh WF generated on the welding bench. A : aluminum<sup>\*</sup>, H : magnetite  $Fe_3O_4$ , M : Manganochromite  $Cr_2MnO_4$ , T : Trevorite  $Fe_2NiO_4$ , J : Jacobsite  $MnFe_2O_4$ , C : Chromite  $Fe_{1,7}Cr_{1,3}O_4$ . \* Aluminum peak corresponds to the filter holder, which is a metallic support in Al.

#### References

- 1 F. Bonthoux, Factors Affecting the Capture Efficiency of a Fume Extraction Torch for Gas Metal Arc Welding, *Ann. Occup. Hyg.*, 2016, **60**, 761–770.
- 2 MétroPol. Method M-274 (Aérosols en fraction inhalable). MetroPol database version 01.1., 2016. Available online:

https://www.inrs.fr/publications/bdd/metropol/fiche.html?refINRS=METROPOL\_274 (accessed on 01 April 2020, original language French).

- 3B. Berlinger, D. G. Ellingsen, M. Náray, G. Záray and Y. Thomassen, A study of the bioaccessibility of welding fumes, *J. Environ. Monit.*, 2008, **10**, 1448.
- 4D. G. Ellingsen, E. Zibarev, Z. Kusraeva, B. Berlinger, M. Chashchin, R. Bast-Pettersen, V. Chashchin and Y. Thomassen, The bioavailability of manganese in welders in relation to its solubility in welding fumes, *Env. Sci Process. Impacts*, 2013, **15**, 357–365.
- 5F. Kastury, E. Smith and A. L. Juhasz, A critical review of approaches and limitations of inhalation bioavailability and bioaccessibility of metal(loid)s from ambient particulate matter or dust, *Sci. Total Environ.*, 2017, **574**, 1054–1074.
- 6O. Butler, D. Musgrove and P. Stacey, Preparation and Certification of Two New Bulk Welding Fume Reference Materials for Use in Laboratories Undertaking Analysis of Occupational Hygiene Samples, *J. Occup. Environ. Hyg.*, 2014, **11**, 604–612.