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Manganese speciation of laboratory-generated welding fumes

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The objective of this laboratory study was to identify and measure manganese (Mn) fractions in chamber-generated welding fumes (WF) and to evaluate and compare the results from a sequential extraction procedure for Mn fractions with that of an acid digestion procedure for measurement of total, elemental Mn. To prepare Mn-containing particulate matter from representative welding processes, a welding system was operated in short circuit gas metal arc welding (GMAW) mode using both stainless steel (SS) and mild carbon steel (MCS) and also with flux cored arc welding (FCAW) and shielded metal arc welding (SMAW) using MCS. Generated WF samples were collected onto polycarbonate filters before homogenization, weighing and storage in scintillation vials. The extraction procedure consisted of four sequential steps to measure various Mn fractions based upon selective solubility: (1) soluble Mn dissolved in 0.01 M ammonium acetate; (2) Mn(0,II) dissolved in 25% (v/v) acetic acid; (3) Mn(III,IV) dissolved in 0.5% (w/v) hydroxylamine hydrochloride in 25% (v/v) acetic acid; and (4) insoluble Mn extracted with concentrated hydrochloric and nitric acids. After sample treatment, the four fractions were analyzed for Mn by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). WF from GMAW and FCAW showed similar distributions of Mn species, with the largest concentrations of Mn detected in the Mn(0,II) and insoluble Mn fractions. On the other hand, the majority of the Mn content of SMAW fume was detected as Mn(III,IV). Although the concentration of Mn measured from summation of the four sequential steps was statistically significantly different from that measured from the hot block dissolution method for total Mn, the difference is small enough to be of no practical importance for industrial hygiene air samples, and either method may be used for Mn measurement. The sequential extraction method provides valuable information about the oxidation state of Mn in samples and allows for comparison to results from previous work and from total Mn dissolution methods.

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Introduction

According to the US Bureau of Labor Statistics, over 300 000 workers in the United States are employed in the welding, brazing and soldering fields.¹ Welding is not a homogenous engineering method to join metal. In addition to the variety of tasks and projects within the field, welding may be performed using numerous processes and operating modes. This paper focuses on three of those processes which can result in significant airborne Mn exposures: short circuit gas metal arc welding (GMAW), flux cored arc welding (FCAW), and shielded metal arc welding (SMAW). All three of these processes produce a weld from heating with an arc between an electrode that provides the filler metal and the metal component(s) to be welded.² With

GMAW, shielding of the weld pool from oxidation is provided from an externally supplied gas mixture. FCAW is shielded by the flux present in the core of the electrode, which often is supplemented by an externally supplied gas or gas mixture. SMAW does not use externally supplied gas(es) for shielding; rather, it is the decomposition of the electrode coating that provides shielding.

The composition of welding fume (WF) is greatly dependent upon the welding process and conditions employed. Using mild carbon steel (MCS) in a chamber study, Zimmer *et al.*³ generated WF using GMAW which contained Fe, Mn, and silica, while FCAW fumes reportedly contained Fe, Mn, silica, Mg, Ca, and Ba. Other researchers have reported that the amount of Mn detected from GMAW fumes ranges from 3–15% (ref. 4–7) of the collected aerosol, with reported concentrations of 0.01–2.7 mg m^{−3}.^{7–9} SMAW fume is reported to contain 3–10% Mn.⁷ In several studies, FCAW was shown to generate the greatest concentration of Mn.^{9–12} The majority of the WF components originate from the electrode,^{2,13} but several other factors may also affect the emission, including the base metal, flux(es), surface coating, shield gases and spattered particles.^{2,7,10,14}

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Additionally, the fume components are not necessarily in the same form or quantities as in the starting materials.¹⁰ Voitkevich,¹⁵ Jenkins *et al.*¹⁶ and Minni *et al.*¹⁷ have reported that the Mn found in WF is primarily in the divalent and trivalent states. Keane *et al.*⁶ found evidence of multiple Mn oxides in GMAW fume by X-ray diffraction, but weak signals from the small particle size limited their absolute identification.

Welding generates a range of health hazards, including noise, heat stress and radiation, but the gases and aerosol particles generated are considered to be the most harmful exposure.² Exposure to WF has been linked to metal fume fever, pneumonitis, airway irritation, lung function changes, skin sensitization, and possible cancers and reproductive effects.^{10,18} While the respiratory system is the primary target of injury, long-term exposure to Mn in WF may lead to disorders of the nervous system.¹⁰ These neurophysical effects may manifest even with relatively low Mn exposures.¹⁹ Results are conflicting as to a link between welding and clinical manganism, a Parkinson's-like neurological disease.^{20–22} However, sub-clinical neurobehavioral changes are consistently reported for workers who experience airborne Mn exposures from metal fumes.^{19,23–26}

After exposure, several factors influence the biological fate (absorption, distribution, metabolism, and elimination) of Mn, such as particle size, shape, solubility and oxidation state. In an animal study, Chen *et al.*²⁷ reported that the Mn oxidation state determines the degree to which this element exerts cytotoxicity. They found Mn³⁺ to be more cytotoxic than Mn²⁺. Therefore, data on the Mn species generated in different operating processes would be valuable to assessing the airborne Mn exposure risks associated with welding. Sequential extraction of welding fume can provide information on the physiochemical availability of Mn. The main objective of our study was to identify and measure Mn species, differentiated by solubility of Mn compounds only, using sequential extraction in laboratory-generated WF collected during GMAW on stainless and mild carbon steels and FCAW and SMAW on mild carbon steel. Additionally, sets of WF samples were analyzed for total, elemental Mn content and the results were compared to the sequential Mn fractions and summation of sequential extraction results.

Experimental

Welding fume generation

Laboratory welding fumes were generated using a welding system within a conical chamber described previously by Keane

*et al.*²⁸ WFs were generated in short circuit mode GMAW using both SS and MCS and with FCAW and SMAW processes using mild carbon steel. Fumes from the weld area were sampled at 200 L min⁻¹ through a 102 mm filter electrostatic medium (Hollingsworth and Vose, East Walpole, MA), cut to fit the filter housing at the top of the chamber. The flow was measured with a mass flow meter (TSI, Shoreview, MN) before sampling. After sampling was completed, filters were removed from the housing, folded inward, weighed to the nearest 0.1 mg and put in sealed anti-static polyethylene bags. Table 1 lists the welding operational conditions used. The gas mixtures used are typical industrial mixtures for the respective steels, while the currents, voltages and other parameters listed are recommended levels for the steel thicknesses used. The available material safety data sheets for the materials used list Mn values typically <5% by weight.

Welding fume collection

Most of the WF particulate matter was recovered from filters at the outlet of the welding chamber by gentle suction onto a 47 mm, 0.8 µm polycarbonate filter (Millipore, Billerica, MA). Fumes were removed from the electrostatic medium with low vacuum so that there was no damage to the filter media and no residue from the filter was present in the recovered fume. Sufficient quantity was collected for metals analysis, but quantitative recovery was not necessary. The collected WF material was then brushed from the polycarbonate filter and its housing using a #3 artist's brush (McMaster-Carr, Aurora, OH) into a tared 75 mm × 75 mm weighing boat. The fume was treated with an anti-static device to prevent losses before and after grinding in a metal-free apparatus to homogenize the sample. Fume was ground using disposable 13 mm × 25 mm polyethylene vials with two 3.2 mm silicon nitride coated ceramic balls and shaken for 30 s in a Wig-L-Bug grinder (Fisher Scientific, Pittsburgh, PA). The material was weighed into 20 mL scintillation vials with polytetrafluoroethylene (PTFE)-lined caps for storage at room temperature.

Sample preparation

Samples (~5 mg) were weighed to the nearest 0.01 mg (*n* = 12 for GMAW on stainless steel and FCAW and SMAW on mild carbon steel; and *n* = 25 for GMAW on mild carbon steel) into extraction tubes. The extraction tubes were 50 mL Maxi-Spin polypropylene centrifuge tubes with 25 mL filter inserts

Table 1 Conditions used in WF generation by welding type

Weld mode	Shield gas (%)	Gas flow (m ³ h ⁻¹)	Wire feed rate (cm min ⁻¹)	Voltage (V)	Current (A)
GMAW-SS	He/Ar/CO ₂ (90/7.5/2.5)	1.13	320	15.5	115
GMAW-MCS	Ar/CO ₂ (75/25)	1.13	320	16	150–160
FCAW-MCS	Ar/CO ₂ (75/25)	1.13	760	26	200
SMAW-MCS	N/A	N/A	17.5 ^a	20	150

^a Rod consumption rate; rod density was 137 g m⁻¹ (measured) GMAW-SS: gas metal arc welding using stainless steel; GMAW-MCS: gas metal arc welding using mild carbon steel; FCAW-MCS: flux cored arc welding using mild carbon steel; SMAW-MCS: shielded metal arc welding using mild carbon steel.

equipped with 0.2 μm polyvinylidene fluoride (PVDF) filters (Grace Davison, Deerfield, IL). Samples were prepared following a sequential extraction procedure based upon work by Thomassen *et al.*,²⁹ with a change made in the final preparation step to allow for possible comparisons to traditional metal dissolution methods, *e.g.*, NIOSH 7303.³⁰ NIOSH 7303 is a hot block dissolution method utilizing concentrated hydrochloric and nitric acids. Digestion methods employing hydrofluoric acid, as used in Thomassen *et al.*,²⁹ are mainly (but not always) applicable to geological samples. For our purposes, owing to safety considerations, such an aggressive digestion procedure was not deemed warranted. Samples were taken through a multiple step extraction and acid dissolution procedure to determine soluble Mn (Step 1); Mn(0) and Mn(II) (Step 2); Mn(III) and Mn(IV) (Step 3); and insoluble Mn (Step 4). Details of the sample preparation procedure are presented in Table 2. Between extraction steps, the samples were centrifuged at 2500 rpm (1260 g) for 15 min in order to filter the extraction solutions for analysis while leaving the welding fume bulk available for subsequent sample preparation steps. Deionized water (18 $\text{M}\Omega\text{ cm}$ resistivity), ammonium acetate (Fisher, Pittsburgh, PA, HPLC grade), glacial acetic acid (Fisher, Pittsburgh, PA, Certified ACS grade), hydroxylamine hydrochloride (Acros Organics, NJ, Reagent ACS grade), and concentrated hydrochloric and nitric acids (both Fisher, Pittsburgh, PA, Trace Metal grade) were used in sample preparation. After Step 1 and after Step 2, the insert section of the extraction tube was transferred to a clean 50 mL polypropylene centrifuge tube. After Step 3, the insert was disassembled and its contents transferred to a clean 50 mL polypropylene centrifuge tube for acid digestion in Step 4. If necessary, samples were filtered between steps using Swinnex® reusable syringe filter holders loaded with 0.45 μm Omnipore™ membrane filters (Millipore, Billerica, MA). Each filter was then placed into the insert holding the bulk sample, thus making the filtered bulk material available for the subsequent extraction/dissolution step(s). If necessary, samples were filtered using Acrodisc® syringe filters with 0.45 μm PTFE membranes (Pall, Port Washington, NY) before analysis of Step 4 solutions.

Quality control (QC) samples of individual Mn compounds were analyzed alongside the WF samples to ensure satisfactory sample preparation and analysis. A solution of manganese nitrate (Inorganic Ventures, Christiansburg, VA) (for

soluble Mn), Mn powder (325 mesh), Mn(II) oxide, and Mn(III) oxide (325 mesh) (all from Sigma-Aldrich, St. Louis, MO), and Mn(IV) oxide (Sigma-Aldrich, St. Louis, MO; 60–230 mesh, Reagent Plus grade), a SiMn alloy material characterized by Thomassen *et al.*,²⁹ (for Mn(0,II) and insoluble Mn), and UK Health and Safety Laboratory (HSL) certified WF materials³¹ HSL MSWF-1 and HSL SSWF-1 were used for QC samples. HSL MSWF-1 and HSL SSWF-1 were collected in ventilation ducts above robotic welding stations.^{32,33} The amount of Mn expected in SiMn alloy was determined by NIOSH 7303 analysis of the bulk material.

Additional sets of laboratory generated WF bulk samples ($n = 3$ for GMAW on stainless steel and FCAW and SMAW on mild carbon steel; and $n = 25$ for GMAW on mild carbon steel) were prepared and analyzed following NIOSH 7303. 2.5 mL concentrated hydrochloric acid were added to the sample in a 50 mL polypropylene tube and the tubes heated at 95 °C for 15 min. After a 5 min cooling step, 2.5 mL concentrated nitric acid were added to the sample tube and the samples heated at 95 °C for 15 min. After cooling, the samples were diluted using deionized water. This method is identical to Step 4 of the sequential method described earlier.

Sample analysis was performed with a Spectro Arcos EOP ICP-AES (Spectro Ametek, Mahwah, NJ).

Statistical analysis

Sample results were tested for outliers using Grubbs' test. The test was performed at the two-sided, 5% significance level. Results identified as outliers were removed based upon laboratory observations, such as early fraction filtration leading to reduced extraction time. To compare the difference between data sets, a one-way ANOVA (in this case, same as a *t*-test) procedure was used. The required normality assumption for the procedure was tested and met. All statistical analyses were performed using SAS Software (version 9.2, SAS Institute Inc., Cary, NC).

Results

The results for the QC samples may be found in Table 3 & 4. Reusable syringe filter holders were used for approximately 30% of the samples (WF and QC) in this study. Their use does not appear to negatively impact the amounts of Mn detected,

Table 2 Conditions for Mn sequential extraction. LOD = limit of detection, LOQ = limit of quantitation

Fraction	Component	Reagent(s)	Conditions	LOD (μg per sample)	LOQ (μg per sample)
1	Soluble Mn	10 mL 0.01 M ammonium acetate	Room temperature, 90 min	0.082	0.274
2	Mn(0) & Mn(II)	10 mL 25% (v/v) acetic acid	75 °C, 90 min	0.025	0.0823
3	Mn(III) & Mn(IV)	10 mL 0.5% (w/v) hydroxylamine hydrochloride in 25% (v/v) acetic acid	75 °C, 90 min	0.29	0.955
4	Insoluble Mn	2.5 mL concentrated hydrochloric acid followed by 2.5 mL concentrated nitric acid	95 °C, two 15 min increments with 5 min cool down between heating steps	0.15	0.514

Table 3 Average ($n = 3$) percent recovery for individual QC samples for each fraction and sum of fractions. Compound stoichiometry used to calculate percent recovery for known Mn compounds and amount of Mn determined using NIOSH 7303 used to calculate percent recovery of SiMn alloy. ND: not detected

Mn compound	Soluble			Insoluble	
	Mn	Mn(0,II)	Mn(III,IV)	Mn	Mn(sum)
Soluble Mn	83.4	8.29	ND	ND	91.7
Mn(0)	3.1	90.7	4.2	0.1	98.2
Mn(II) oxide	<0.1	101.0	1.5	<0.1	102.6
Mn(III) oxide	<0.1	1.1	81.7	5.1	88.1
Mn(IV) oxide	ND	<0.1	86.7	3.0	89.9
SiMn alloy	0.6	40.2	1.4	32.9	75.1

as determined by quantitative QC recoveries and WF results in agreement with those from WF samples that did not need filtration. For the Mn compounds, the samples recovered at 82% or higher in the expected fraction and mass balance was found using Mn(sum). Because the low pH of the second extraction solution could partially attack the compounds to be extracted in the third step,³⁴ Mn(sum) is the most telling indication of the cumulative recovery using the sequential method. These overall results confirm the suitability of the method for Mn compounds of known valence and stoichiometry.

For the SiMn alloy, 40.2% of the expected Mn was detected as Mn(0,II) and 32.9% was detected as insoluble Mn. Overall, 75.1% of the expected Mn in SiMn alloy was recovered. For the stainless steel WF certified bulk (HSL-SSWF-1), 74.1% was recovered using Mn(sum) and the largest fraction measured was Mn(0,II). For the mild steel WF certified bulk (HSL-MSWF-1), 68.2% was recovered and the greatest fraction was insoluble Mn. Using NIOSH 7303 as a reference, HSL-SSWF-1 and HSL-MSWF-1 were recovered at 84.8% and 96.8%, respectively. Detectable amounts of soluble Mn were found in 3 of the 6 HSL-MSWF-1 bulk samples analysed; therefore, the results shown for the soluble Mn fraction are an average of the three measurable results.

Fig. 1 shows the Mn content obtained for each of the generated WF. The average results of the Mn speciation analysis from the lab generated WF as mg Mn per g of bulk fume are shown. FCAW on mild carbon steel produced the greatest

Table 4 Average concentration of Mn fractions detected (% m/m) \pm SD for certified WF bulks³¹

	HSL-SSWF-1 ($n = 3$)	HSL-MSWF-1 ($n = 6$)
	% m/m	% m/m
Soluble Mn	0.619 ± 0.17	0.013 ± 0.0092^a
Mn(0,II)	8.57 ± 0.46	0.20 ± 0.0079
Mn(III,IV)	4.68 ± 0.43	0.36 ± 0.073
Insoluble Mn	3.08 ± 0.48	0.45 ± 0.10
Mn(sum)	17.0 ± 0.58	1.01 ± 0.098
Certified amount	22.9	1.48
%Recovery	74.1	68.2

^a $n = 3$.

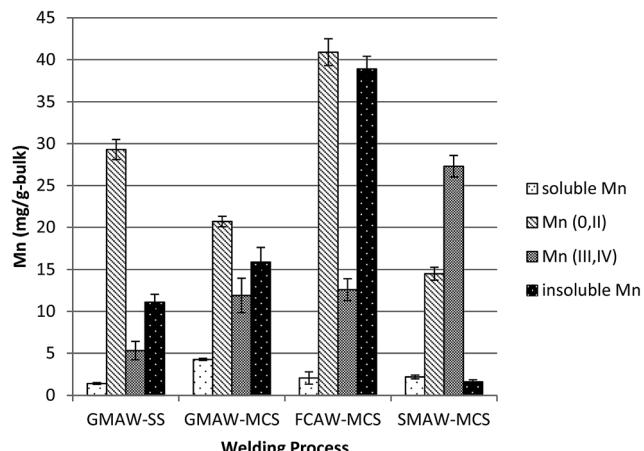


Fig. 1 Manganese fractions (mg g^{-1}) detected in laboratory-generated WF for different welding processes (error bars are standard deviations).

overall Mn concentration, with 94.4 mg Mn per g measured (summation of the 4 steps). The next highest concentration of Mn per g of bulk fume was generated using GMAW of MCS with 52.8 mg Mn per g. The amount of Mn detected from GMAW-SS did not differ significantly from that detected with SMAW-MCS, 47.1 mg Mn per g and 45.6 mg Mn per g of bulk fume, respectively.

In comparing results from GMAW fume only, more soluble Mn, Mn(III,IV) and insoluble Mn are detected (leading to greater overall Mn measured) when mild carbon steel was the base material. When welding with stainless steel, more proportional mass of Mn(0,II), relative to the bulk fume mass was detected than when mild carbon steel was the base material. Greater Mn(sum) was detected with GMAW-MCS than with GMAW-SS and this difference in the Mn(sum) detected for GMAW fumes was found to be statistically significant. However, regardless of material welded, the prevalence of Mn fractions in GMAW fume remained the same: Mn(0,II) > insoluble Mn > Mn(III,IV) > soluble Mn (Fig. 2). For FCAW-MCS, this same ordinal rank was observed but the difference between Mn(0,II) and insoluble Mn was much

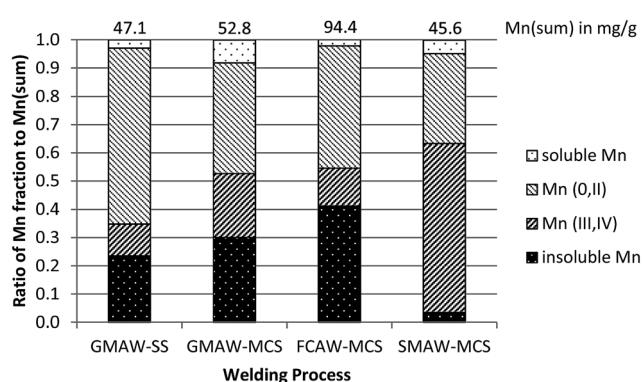


Fig. 2 Ratio of Mn fractions to bulk fume total mass for four welding processes.

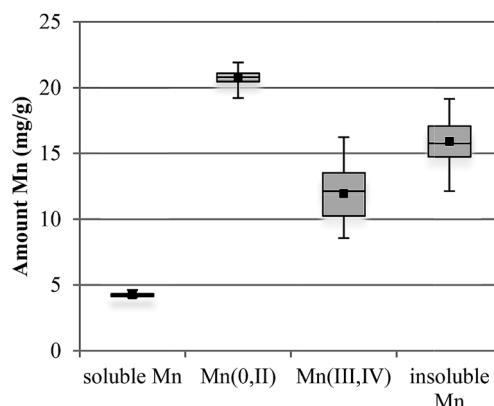


Fig. 3 Box plot of Mn detected (mg g^{-1}) for generated GMAW-MCS fume ($n = 24$). One outlier removed for each fraction.

smaller than with GMAW fume, however, the difference was still statistically significant. The order of prevalence for SMAW was $\text{Mn(III,IV)} > \text{Mn(0,II)} > \text{soluble Mn}$ and insoluble Mn . No statistically significant difference was found between soluble Mn and insoluble Mn for SMAW-MCS fume.

The fraction of Mn detected when welding in either short circuit GMAW or SMAW was approximately 5% of the total weight of the bulk WF. FCAW yielded the highest overall Mn result, with 9.44% of the total weight of the bulk WF attributed to Mn. FCAW also gave the greatest Mn(0,II) and insoluble Mn weight concentrations. These Mn concentrations were between

2 to 2.8 times and 2.4 to 24 times, respectively, of that of GMAW-MCS and SMAW.

Three GMAW-MCS results were identified as outliers, but only one sample was removed from the data set based upon laboratory observations. Fig. 3 displays a boxplot to show the distribution of the data upon removal of the outlier. The distribution of the results was largest for fractions 3 & 4 (Mn(III,IV) and insoluble Mn), indicating that there is greater variability for these later extraction steps.

Boxplots comparing the sequential and hot block methods are shown in Fig. 4 for each type of generated WF. Outliers are included in Fig. 4. As expected due to additional error involved with multiple extraction steps, there is a greater spread in the total Mn results for the sequential method when compared with the hot block method. Also, the loss of Mn during sample handling is evident in the reduced amount of Mn recovered from the GMAW-MCS WF using the summation of the Mn fractions in the sequential method compared to that recovered using the hot block method.

The overall percentage of Mn detected in GMAW-MCS using the sequential method was 5.28% Mn and was 5.65% using the hot block acid dissolution method (NIOSH 7303). To compare the difference between these two analytical procedures, statistical analyses were performed for all data including the outliers as well as for data excluding the outliers. The hot block method gave statistically significantly higher mean results than those of the sequential method ($p < 0.001$).

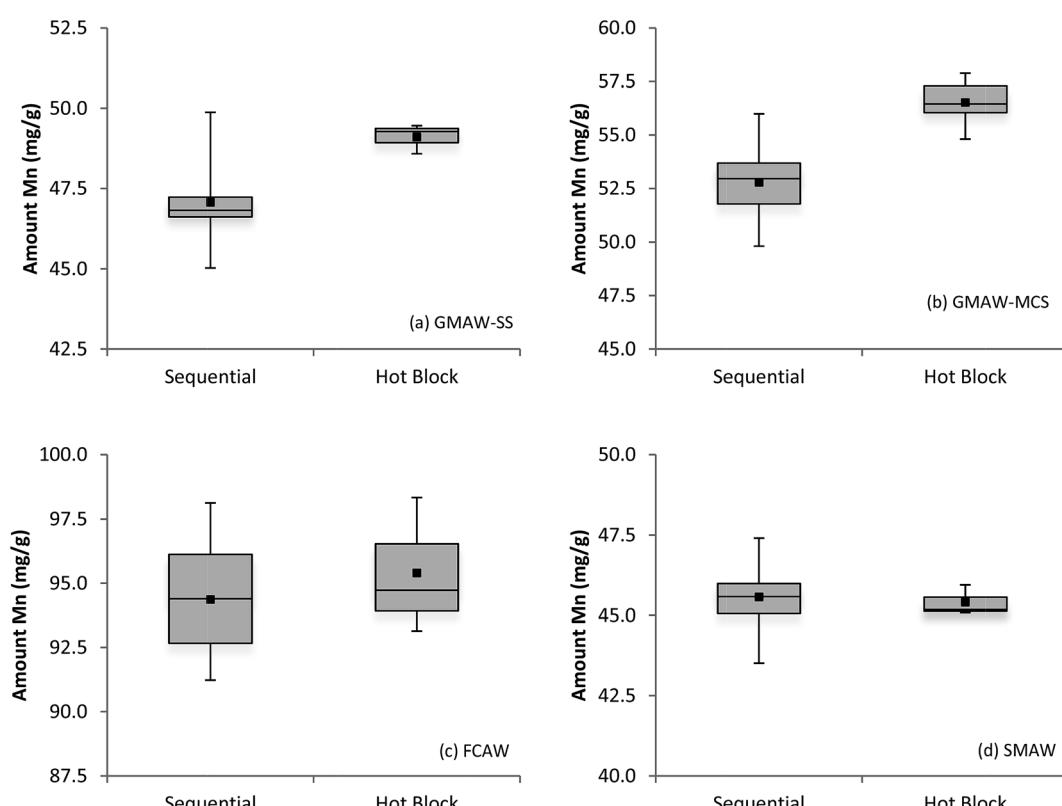


Fig. 4 Boxplots of total Mn detected (mg g^{-1}) in generated (a) GMAW-SS*, (b) GMAW-MCS ($n = 25$), (c) FCAW*, and (d) SMAW* fumes for sequential and hot block methods * $(n = 12$ for sequential; $n = 3$ for hot block).

Discussion

The results of Fig. 4 show that the sums of Mn amounts obtained by sequential extraction are comparable to the amounts of Mn measured using NIOSH 7303. These data are demonstrative of the ruggedness of the sequential extraction procedure. Approximately 70% of the certified amount of Mn was detected in the UK HSL certified WF samples using the sequential extraction method. The sample preparations recommended in the certification reports use stronger acids and more aggressive conditions to prepare the certified WF than were used in the last step of the sequential method. A “total” digestion of the WF sample is not warranted in light of the relevance of soluble Mn components on uptake in the body.^{35,36} Ellingsen *et al.*³⁷ reported a univariate correlation between soluble Mn in aerosol samples and Mn levels in urine and blood of welders using a relatively mild extraction of WF in an artificial lung lining simulant (Hatch Solution) at 37 °C. Also, a stronger acid digestion procedure was not used in the sequential method to ultimately allow the WF Mn(sum) results to be compared to historical results that have utilized NIOSH 7303 (and equivalent methods) for Mn measurement. NIOSH 7303 and comparable methods are of interest for purposes of comparison since it is these methods, *i.e.*, those that do not employ HF in their dissolution procedures, which are widely used by occupational hygiene laboratories worldwide.

The distribution pattern of Mn species detected was similar for WF generated using GMAW for both stainless steel and mild carbon steel base materials, with Mn(0,II) > insoluble Mn > Mn(III,IV) > soluble Mn. This distribution pattern is not in agreement with that reported by Berlinger *et al.*⁸ In that study, relatively similar proportions of Mn were detected in the insoluble and soluble Mn/Mn(0,II) fractions, whereas, our results show 1.6 and 2.8 times more soluble Mn/Mn(0,II) than insoluble Mn for GMAW-MCS and GMAW-SS, respectively. The overall percent Mn content was slightly elevated for GMAW-generated fume when mild carbon steel was used as the base material *versus* when using stainless steel as the base metal (5.3% vs. 4.7%, respectively). A similar effect has been reported by Pesch *et al.*¹¹ and Lehnert *et al.*¹³ The differences in Mn content in our study may have been due to differences in the shield gases and current applied. While the conditions were appropriate for the base material used, more CO₂ was present in the shield gas mixture and a higher current was applied when using MCS. Both of these factors have been shown to increase particle number concentration³⁸ and fuming.¹⁰

The greater spread of results shown in Fig. 4 for the sequential method is due to the complicated nature of the sample preparation procedure. More preparation steps yields more potential sources of error and this error is propagated due to the sequential nature of the method. The sequential method was performed over the course of 4 days, but the NIOSH 7303 sample preparation process can be completed in a few hours. This greater amount of time for sample preparation increases the chance of sample loss. Additionally, for bulk samples, the Mn results may be lower than those from total elemental methods due to difficulties in quantitatively transferring bulk

material from the tube insert to a digestion vessel. While Steps 1 through 3 take place in a single extraction vessel insert, Step 4 requires the removal of the sample (and any filters used throughout the extraction) into a new tube for the acid digestion. The complete removal of the bulk sample can be problematic and it is highly likely that a small portion of the undissolved sample residue is unable to be transferred through a deionized water rinse. This increases the sample error and variability for the 4th step and prevents the entire remaining undissolved fraction from being available for acid digestion and analysis. Consequently the measured Mn(sum) is slightly less than what should ideally be obtained for total, elemental Mn using the hot block acid dissolution method *via* NIOSH 7303. The results shown for the SiMn alloy and the UK HSL certified WF illustrate this point. The amount of Mn in the SiMn alloy was determined using NIOSH 7303, but the lower than expected Mn(sum) recovery for that alloy is due to sample loss when the sample residue was transferred for the final extraction step. With the sequential method, 74.1% of HSL-SSWF-1 and 68.2% of HSL-MSWF-1 were recovered, but an additional 10–30% was recovered using the hot block method alone. Based upon the summation of the laboratory-generated WF results from the sequential steps and the hot block method results, it was found that over 90% of the bulk material was successfully transferred for the fourth step of the sequential method in this study. This is not expected to be an issue for filter based field samples because the fume will deposit onto the filter, easing its transfer to the subsequent extraction and digestion vessels.

In comparing GMAW to the other two welding processes (*i.e.*, FCAW and SMAW) with mild carbon steel used in this study, either the overall concentration of Mn detected or the distribution of Mn species varied. FCAW and GMAW showed similar ratio distributions of Mn fractions; however, the overall weight percentage of Mn detected in FCAW is nearly double than that detected using GMAW. This is supportive of the results of Lehnert *et al.*¹³ and Wallace *et al.*,¹² who found that the mass concentration of Mn for FCAW was 2–4 times greater than for GMAW. On the other hand, SMAW yielded the lowest Mn content, and its species distribution was unique, with the majority of its Mn content detected as Mn(III,IV). In a field study using stationary air samples, Berlinger *et al.*⁸ found SMAW to have a greater Mn content than that of GMAW for unalloyed structural steel, *i.e.* MCS, and corrosion-resistant steels, *i.e.* SS, but the fractional distribution for SMAW (with Mn(III,IV) as the dominant fraction) agrees with our laboratory results.

For all of the welding processes studied, the most prevalent Mn fractions were those of Mn(0,II) and Mn(III,IV). Observation of the prevalence of the Mn(0,II) fraction in WF was reported by Thomassen *et al.*,²⁹ in agreement with our results. Other workers have reported predominance of soluble and sparingly soluble Mn fractions, in agreement with our data. For instance, Voitkevich¹⁵ reported that Mn(II) and Mn(III) are the most probable oxidation states in WF, which is consistent with the results reported here. The fractionation method does not separate the fractions into individual oxidation states, but rather according to solubility. This enables potential linkage to investigations of Mn bioavailability,³⁷ which is of interest for

toxicology studies.^{2,4,27,36} It also relies on the material being extracted in a sequential fashion that may not be amenable to WF particles due to their complicated structure.^{17,39} Therefore, any identification of specific Mn compounds in WF is not possible with this method. These limitations need to be considered when applying the method to WF.

Conclusions

While the difference in the sequential extraction and hot-block dissolution methods is statistically significant, the results for Mn(sum) are indeed quite comparable (53 mg g⁻¹ vs. 57 mg g⁻¹). This difference is small enough to have no practical importance and either method may be used for Mn measurement in industrial hygiene samples. The sequential extraction method has been validated at an independent laboratory and utilized for over 600 field samples. While the sequential extraction method is time- and labor-intensive, it provides valuable information on the Mn fractionation of samples. Due to the role solubility and oxidation state play in the biological fate of metal compounds, this information could provide insight into bioavailability and toxicity of Mn from welding fume and other occupational exposures and aid health hazard evaluations.

Disclaimers

The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health. Mention of any company or product does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH). In addition, citations to Web sites external to NIOSH do not constitute NIOSH endorsement of the sponsoring organizations or their programs or products. Furthermore, NIOSH is not responsible for the content of these Web sites. All Web addresses referenced in this document were accessible as of the publication date.

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Notes and references

1 U.S. Bureau of Labor Statistics, Division of Occupational Employment Statistics, Occupational Employment and Wages, May 2014, <http://www.bls.gov/oes/current/oes514121.htm>, accessed May 4 2015.

- 2 J. M. Antonini, *Crit. Rev. Toxicol.*, 2003, **33**, 61–103.
- 3 A. T. Zimmer and P. Biswas, *J. Aerosol Sci.*, 2001, **32**, 993–1008.
- 4 J. M. Antonini, K. Sriram, S. A. Benkovic, J. R. Roberts, S. Stone, B. T. Chen, D. Schwegler-Berry, A. M. Jefferson, B. K. Billig, C. M. Felton, M. A. Hammer, F. Ma, D. G. Frazer, J. P. O'Callaghan and D. B. Miller, *Neurotoxicology*, 2009, **30**, 915–925.
- 5 D. E. Hilton and P. N. Plumridge, *Weld. Met. Fabr.*, 1991, **59**, 555–560.
- 6 M. Keane, S. Stone and B. Chen, *J. Environ. Monit.*, 2010, **12**, 1133–1140.
- 7 W. A. Burgess, in *Recognition of Health Hazards in Industry: A Review of Materials and Processes*, 2nd edn, 1995, pp. 167–204.
- 8 B. Berlinger, M. Naray, I. Sajo and G. Zaray, *Ann. Occup. Hyg.*, 2009, **53**, 333–340.
- 9 F. Taube, *Ann. Occup. Hyg.*, 2013, **57**, 6–25.
- 10 NIOSH, Criteria for a Recommended Standard Welding, Brazing, and Thermal Cutting, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Publication No. 88–110, 1988.
- 11 B. Pesch, T. Weiss, B. Kendzia, J. Henry, M. Lehnert, A. Lotz, E. Heinze, H. U. Kafferlein, R. Van Gelder, M. Berges, J.-U. Hahn, M. Mattenkrott, E. Punkenburg, A. Hartwig, T. Bruning and T. W. Group, *J. Exposure Sci. Environ. Epidemiol.*, 2012, **22**, 291–298.
- 12 M. Wallace, S. Shulman and J. Sheehy, *Appl. Occup. Environ. Hyg.*, 2001, **16**, 771–779.
- 13 M. Lehnert, B. Pesch, A. Lotz, J. Pelzer, B. Kendzia, K. Gawrych, E. Heinze, R. van Gelder, E. Punkenburg, T. Weiss, M. Mattenkrott, J.-U. Hahn, C. Moehlmann, M. Berges, A. Hartwig, T. Bruening and G. Weldox Study, *Ann. Occup. Hyg.*, 2012, **56**, 557–567.
- 14 C. N. Gray and P. J. Hewitt, *Ann. Occup. Hyg.*, 1982, **25**, 431–438.
- 15 V. Voitkevich, *Welding Fumes: Formation, Properties and Biological Effects*, Abington Publishing, Cambridge, England, 1995.
- 16 N. T. Jenkins and T. W. Eagar, *Weld. Res.*, 2005, 87-s–93-s.
- 17 E. Minni, T. E. Gustafsson, M. Koponen and P.-L. Kalliomaki, *J. Aerosol Sci.*, 1984, **15**, 57–68.
- 18 J. M. Antonini, A. B. Lewis, J. R. Roberts and D. A. Whaley, *Am. J. Ind. Med.*, 2003, **43**, 350–360.
- 19 W. Laohaudomchok, X. Lin, R. F. Herrick, S. C. Fang, J. M. Cavallari, R. Shrairman, A. Landau, D. C. Christiani and M. G. Weisskopf, *Neurotoxicology*, 2011, **32**, 171–179.
- 20 A. B. Santamaria, C. A. Cushing, J. M. Antonini, B. L. Finley and F. S. Mowat, *J. Toxicol. Environ. Health, Part B*, 2007, **10**, 417–465.
- 21 M. R. Flynn and P. Susi, *Int. J. Hyg. Environ. Health*, 2009, **212**, 459–469.
- 22 J. Jankovic, *Neurology*, 2005, **64**, 2021–2028.
- 23 R. M. Park, *Saf. Health Work*, 2013, **4**, 123–135.
- 24 R. M. Bowler, W. Koller and P. E. Schulz, *Neurotoxicology*, 2006, **27**, 327–332.

25 R. M. Bowler, S. Nakagawa, M. Drezgic, H. A. Roels, R. M. Park, E. Diamond, D. Mergler, M. Bouchard, R. P. Bowler and W. Kollerg, *Neurotoxicology*, 2007, **28**, 298–311.

26 D. Mergler, G. Huel, R. Bowler, A. Iregren, S. Belanger, M. Baldwin, R. Tardif, A. Smargiassi and L. Martin, *Environ. Res.*, 1994, **64**, 151–180.

27 J.-Y. Chen, G. C. Tsao, Q. Zhao and W. Zheng, *Toxicol. Appl. Pharmacol.*, 2001, **175**, 160–168.

28 M. Keane, A. Siert, S. Stone, B. Chen, J. Slaven, A. Cumpston and J. Antonini, *Weld. J.*, 2012, **91**, 241-s–246-s.

29 Y. Thomassen, D. G. Ellingsen, S. Hetland and G. Sand, *J. Environ. Monit.*, 2001, **3**, 555–559.

30 NIOSH, Elements by ICP (Hot Block/HCl/HNO₃) Digestion (Method 7303) in NIOSH Manual of Analytical Methods, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health (NIOSH), Cincinnati, OH, 4th edn, Publication No. 94–113, 1994.

31 O. Butler, D. Musgrove and P. Stacey, *J. Occup. Environ. Hyg.*, 2014, **11**, 604–612.

32 UK Health and Safety Laboratory (HSL), Certification Report: Reference Material HSL SSWF-1 Elements in Mild Steel Welding Fume, <http://www.hsl.gov.uk/media/231817/20.pdf>, accessed May 4 2015.

33 UK Health and Safety Laboratory (HSL), Certification Report: Reference Material HSL MSWF-1 Elements in Mild Steel Welding Fume, <http://www.hsl.gov.uk/media/231751/hsl%20mswf-1%20certification%20sheet%20v1%20final.pdf>, Accessed May 4 2015.

34 A. Tessier, P. G. C. Campbell and M. Bisson, *Anal. Chem.*, 1979, **51**, 844–851.

35 D. G. Ellingsen, S. Hetland and Y. Thomassen, *J. Environ. Monit.*, 2003, **5**, 84–90.

36 K. Sriram, G. X. Lin, A. M. Jefferson, J. R. Roberts, O. Wirth, Y. Hayashi, K. M. Krajnak, J. M. Soukup, A. J. Ghio, S. H. Reynolds, V. Castranova, A. E. Munson and J. M. Antonini, *FASEB J.*, 2010, **24**, 4989–5002.

37 D. G. Ellingsen, E. Zibarev, Z. Kusraeva, B. Berlinger, M. Chaschin, R. Bast-Pettersen, V. Chaschin and Y. Thomassen, *Environ. Sci.: Processes Impacts*, 2013, **15**, 357–365.

38 A. T. Zimmer, P. A. Baron and P. Biswas, *J. Aerosol Sci.*, 2002, **33**, 519–531.

39 P.-L. Kalliomaki, A. Grekula, J. Hagberg and S. Sivonen, *J. Aerosol Sci.*, 1987, **18**, 781–784.