# Development of a field method for measuring manganese in welding fume

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Workers who perform routine welding tasks are potentially exposed to fume that may contain manganese. Manganese may cause respiratory problems and is implicated in causing the occurrence of Parkinson-like symptoms. In this study, a field colorimetric method for extracting and measuring manganese in welding fume was developed. The method uses ultrasonic extraction with an acidic hydrogen peroxide solution to extract welding fume collected on polyvinyl chloride filters. Commercially available pre-packaged reagents are used to produce a colored solution, created by a reaction of manganese(II) with 1-(2-pyridylazo)-2-naphthol. Absorbance measurements are then made using a portable spectrophotometer. The method detection limit and limit of quantification (LOQ) were 5.2 µg filter<sup>-1</sup> and 17 µg filter<sup>-1</sup>, respectively, with a dynamic range up to 400 µg filter<sup>-1</sup>. When the results are above the LOQ for the colorimetric method, the manganese masses are equivalent to those measured by the International Organization for Standardization Method 15202-2, which employs a strong acid digestion and analysis using inductively coupled plasma-optical emission spectrometry.

#### Introduction

Welders may be exposed to a wide variety of hazardous substances while performing routine welding tasks. <sup>1,2</sup> The fume that is generated during welding is a complex mixture of metal oxides that condense from the gas phase to form very small particles. <sup>3</sup> The composition of the fume depends upon the type of welding process used and the chemical composition of the metals being joined. A wide variety of methods are used to join metals together. Some of the more common types are shielded manual metal arc welding (SMAW), gas metal arc welding (GMAW), and flux-cored arc welding (FCAW). In FCAW and SMAW, fluxes are incorporated into the consumable electrodes to shield against atmospheric gases. <sup>1,2</sup> Manganese may be present in both the flux material and the metal electrodes.

Welding fume may contain irritants and can be toxic to the respiratory system, possibly causing pulmonary edema, chronic bronchitis, emphysema, pneumonia, asthma, welder's lung, and metal fume fever. Manganese is one of the components of welding fume that may have serious effects on health. Some studies have shown that welders exposed to fumes that contains manganese may have an increased risk of developing Parkinson-like symptoms, while other studies have found no linkage. These symptoms include a fixed gaze, bradykinesia, postural difficulties, rigidity, tremor, dystonia, and decreased mental status. Other studies have shown

In the United Stated, there are currently three workplace exposure limits for manganese. The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for manganese is 1 mg m<sup>-3</sup> as an 8 h time-weighted average (TWA), and 3 mg m<sup>-3</sup> as a short-term exposure limit. <sup>14</sup> The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) is 5 mg m<sup>-3</sup> (ceiling limit). <sup>14</sup> The American Conference of Governmental Industrial Hygienists (ACGIH) has established a threshold limit value (TLV) of 0.2 mg m<sup>-3</sup> for manganese. <sup>15</sup>

In the current analytical methods for determining the quantity of manganese in welding fume, a sample of the particles in workplace air is collected on polyvinyl chloride (PVC) filters or mixed cellulose ester (MCE) filters mounted in plastic cassettes. Samples are collected using a personal sampling pump at a flow rate of 2 L min<sup>-1</sup>, over a period of 8 h. The sample is sent to an accredited laboratory for an analysis of the total manganese content using strong acid digestion and measurement by inductively coupled plasma-optical emission spectrometry (ICP-OES). 16,17 The process typically requires 4-6 weeks from the time the samples are collected until the results of the analysis are reported. With this turnaround time, it is difficult to relate work practices to exposure levels in a timely fashion. The ability to measure manganese in welding fume within 24 h would allow managers, supervisors, and/or safety personnel to communicate exposure levels to workers and take corrective actions to reduce exposure.

The goal of this study was to develop a rapid field method for measuring manganese in welding fume. HACH<sup>®</sup> method 8149<sup>18</sup> is a colorimetric method for determining manganese in water and wastewater. By adapting this method, the manganese is extracted from the filters and converted to the soluble manganese(II) form. An ultrasonic bath is used to extract the

that chronic exposure to elevated manganese levels in the workplace results in increased respiratory problems. 11-13

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fume into an acidic solution of hydrogen peroxide. After dissolution, 1-(2-pyridylazo)-2-naphthol (PAN) indicator is added to the solution; it combines with manganese to form an orange-colored complex. The absorbance is then measured on a spectrophotometer. In order to ensure that the new extraction procedure was accurate, precise, and compatible with the HACH<sup>®</sup> method, a series of experiments were conducted to evaluate analytical recovery, stability, method detection limit, and interferences.

# **Experimental**

#### Air sample generation and collection

Welding fume samples were collected on PVC filters (37 mm, 5.0 µm pore size, with cellulose backup pad, SKC, Inc., Eighty Four, Pennsylvania, USA) using a custom-made multiport sampler. The multiport sampler was connected to a high-volume (15 L min<sup>-1</sup>) air sampling pump (Gilian AirCon2, West Caldwell, New Jersey, USA) and it collected eight samples simultaneously with a measured flow rate of 1.7 (±0.1) L min<sup>-1</sup> for each individual port. All welding was performed on soft steel using SMAW. Three types of electrodes were used: UTP 711B (<1% Mn; Bohler Thyssen Welding, Stafford, Texas, USA); E11018-M (<5% Mn; Hobart Welding Products, Appleton, Wisconsin, USA); and ArcTec 41 (16% Mn; ArcTec Alloys Ltd, Calgary, Alberta, Canada).

#### Materials and equipment

For some experiments, the PVC filters were placed into 15 mL centrifuge tubes (Falcon, Becton-Dickinson, Franklin Lakes, New Jersey, USA). The addition of reagents and deionized water was performed with a mechanical pipette (Rainin Instrument Company, Inc., Franklin Lakes, New Jersey, USA). A vortex mixer (Barnstead International, Dubuque, Iowa, USA) was used to mix the samples prior to extraction in the ultrasonic bath (117-V, 50 Hz, Crest Ultrasonics, Trenton, New Jersey, USA). An aliquot of the extraction solution was transferred to a HACH<sup>®</sup> 25 mL sample cell (2.0 cm path length) with cap (Loveland, Colorado, USA) and diluted to 10 mL. After the HACH<sup>®</sup> reagents were added, the absorbance was measured using a DR/2400 spectrophotometer (HACH<sup>®</sup> Company, Loveland, Colorado, USA).

For other experiments, the PVC filters were placed into 25 mL beakers (Fisher Scientific, Hampton, New Hampshire, USA) and sequentially digested with concentrated nitric and hydrochloric acids on a hot-plate (VWR International, Inc., West Chester, Pennsylvania, USA). These samples were analyzed using an ICP-OES (Applied Research Laboratories 34 000, Sunland, California, USA). The ICP-OES is a simultaneous side-view instrument with a pneumatic nebulizer for sample introduction. The ICP-OES method detection limit for manganese is 0.5 μg L<sup>-1</sup> for the conditions and instrument used for this study. An analytical balance (Mettler Toledo, model XS105, Columbus, Ohio, USA) was used for weighing.

#### Reagents and solutions

A 1000 mg  $L^{-1}$  multielement standard solution (Mn, Fe, Zn, Mg, Ca, Cu, Pb, Ti, Co, Ni, Cr) and a 1000 mg  $L^{-1}$  Mn

solution (SPEX CertiPrep standard solution in 2% nitric acid, Metuchen, New Jersey, USA) were used to prepare spiking, standard, and calibration check solutions. Iron solutions at 1000 mg L<sup>-1</sup> were prepared by dissolving analytical grade ferrous ammonium sulfate (EM Science, Cherry Hill, New Jersey, USA) and ferric nitrate nonahydrate (JT Baker, Mallinckrodt Baker, Inc., Phillipsburg, New Jersey, USA) in deionized water (18 MΩ, Millipore Milli-Q Plus, Molsheim, France). Analytical grade manganese(IV) oxide was obtained from JT Baker (Mallinckrodt Baker, Inc., Phillipsburg, New Jersey, USA). Nitric, hydrochloric, and sulfuric acids were obtained from OPTIMA (Seastar Chemicals Inc., Pittsburgh, Pennsylvania, USA). The 50% hydrogen peroxide solution, ascorbic acid powder pillows, alkaline cyanide reagent, and PAN indicator solution were obtained from HACH® (Loveland, Colorado, USA).

# **Experimental methods**

## Acidic hydrogen peroxide extraction and colorimetric analysis

The field method for measuring manganese in welding fume was evaluated by measuring the recovery of manganese that was added to PVC filters in one of three ways. In the first procedure, the PVC filters were placed into 15 mL centrifuge tubes and solid manganese(IV) oxide was weighed directly onto the filters. In the second method, known concentrations of manganese(II) in solution were pipetted onto the PVC filters in the 15 mL centrifuge tubes. In the third technique, welding fumes were collected on PVC filters in cassettes using a multiport sampler with a high-volume pump.

The filters were then analyzed using the colorimetric method as follows. The cassettes were opened and the filters were transferred to 15 mL centrifuge tubes. Two millilitres of deionized water were added, followed by 0.5 mL of 6 M sulfuric acid and 3.0 mL of 3% hydrogen peroxide. The tubes were capped and the contents were mixed using a vortex mixer, ensuring that the filters were completely submerged in the extraction solution. The centrifuge tubes were placed in an ultrasonic bath and the filters were extracted for 30 min. In order to allow for complete dissolution of the manganese, the samples were allowed to set in the acidic hydrogen peroxide extraction solution for a minimum of 2 h before analysis. After extraction, 4.5 mL of deionized water was added to the centrifuge tubes and the contents were mixed using the vortex mixer. An aliquot of the extraction solution in each of the centrifuge tubes (100 µL to 250 µL depending on the expected manganese concentration) was transferred to a HACH® 25 mL sample cell with cap, and diluted to 10.0 mL with deionized water. Ascorbic acid was added from a powder pillow, followed by 15 drops of alkaline-cyanide reagent, and 21 drops of PAN indicator solution. After the addition of each reagent, the sample cells were capped and inverted to mix. The color was allowed to develop for twelve minutes before the absorbance was measured at 560 nm using a spectrophotometer. The absorbance was compared with five matrix-matched calibration solutions that were prepared daily, ranging from  $0 \text{ mg L}^{-1}$  to  $0.70 \text{ mg L}^{-1}$ .

# ISO method 15202-2—strong acid digestion and ICP-OES analysis

The ISO method 15202-2 was the standard reference method against which the accuracy of the colorimetric method was compared.<sup>17</sup> Total manganese in the welding fume collected on the filters was measured according to the sequential digestion procedure in nitric and hydrochloric acids described in the ISO method. The solution was analyzed using an ICP-OES.

An ICP-OES blank solution was prepared in 5% hydrochloric acid and the matrix-matched standard solution was prepared at 10 mg  $L^{-1}$  of manganese. Calibration check solutions were independently prepared at 1.0 mg  $L^{-1}$  and 5.0 mg  $L^{-1}$  in 5% hydrochloric acid. For all measurements, the calibration check solutions were within  $\pm 5\%$  of the standard value. During the evaluation of potential interferences from other constituents in welding fume, a standard solution was prepared in 5% hydrochloric acid at 10 mg  $L^{-1}$  of manganese, iron, zinc, magnesium, calcium, copper, lead, titanium, cobalt, nickel, and chromium. A calibration check solution was independently prepared at 1.0 mg  $L^{-1}$  in 5% hydrochloric acid. For all measurements, the calibration check solution was within  $\pm 10\%$  of the standard value for all elements.

## Results and discussion

NIOSH guidelines for the evaluation of workplace air sampling and analysis methods recommend that a suite of experiments be conducted to validate the method under investigation.<sup>19</sup> The recovery of an analyte from the sampling medium is evaluated by adding known quantities of an analyte to a filter and measuring the quantity that can be recovered. With the data from the recovery experiment, the bias (*B*) can be calculated from:

$$B = [(\mu/T) - 1],$$

where  $\mu$  is the measured mean and T is the true concentration of the spike.

The bias must be less than 10% at all spiking levels. For a method to meet the NIOSH accuracy criteria, the recovery of the analyte from the filter media should be greater than or equal to 75% of the true concentration at least 95% of the time.

In the high temperature, oxidizing environment that is present during particle formation in welding fume, the manganese is expected to be present as mixed manganese oxide compounds (manganese(II) manganese(III) oxide and manganese(IV) oxide). These compounds must be dissolved before analysis by colorimetry. The standard methods for analysis of welding fume use strong acids and high temperatures to reduce and dissolve the manganese compounds that may be present. The vapors generated during dissolution require the use of chemical fume hoods. To avoid using strong acid digestion, a field method requires a different dissolution process. An evaluation of standard reduction potentials indicates that hydrogen peroxide in acidic solution is an adequate reducing agent according to the equation: <sup>21</sup>

$$MnO_2(s) + 2H^+ + H_2O_2(aq) \leftrightharpoons Mn^{2+} + O_2(g) + 2H_2O(l)$$
  
 $E^\circ = 0.53 \text{ V}$ 

Preliminary experiments that were performed to evaluate the kinetics of the reaction gave quantitative recoveries (93–105%) for manganese(IV) oxide on PVC filters. These results demonstrated that an acidic hydrogen peroxide solution is capable of reducing insoluble manganese(IV) oxide to soluble manganese(III) that is available to react with PAN.

The method published by HACH<sup>®18</sup> uses two minutes for color development. A stability experiment showed that in the presence of the acidic hydrogen peroxide extraction solution, the length of time for stable color development needed to be increased to twelve minutes. The residual hydrogen peroxide present in the extraction solution depresses the absorbance of the orange-colored complex that is produced from the reaction of manganese with PAN; therefore, the calibration solutions must be matrix-matched to the samples.

To measure the accuracy and precision of the method, six replicates of manganese(II) ion in solution were pipetted onto PVC filters at 0.1, 0.5, 1.0, and 2.0 times the TLV for manganese based on an 8 h TWA and a sampling flow rate of 2 L min<sup>-1</sup>. Under these conditions for filter collection, the loading of a filter at the TLV is 190  $\mu$ g filter<sup>-1</sup>. These samples were extracted and analyzed using the colorimetric method, after which the percent recovery of the manganese was calculated. The results show that the new colorimetric method satisfies the desired performance criteria (Table 1). In all samples, manganese recovery was greater than 97% and the absolute bias at all levels was <3%.

A group of PVC filters, loaded with fume from the UTP 711B electrode (<1% Mn), were prepared for the limit of detection (LOD) evaluation<sup>19</sup> by spiking aliquots of manganese(II) solution onto the prepared fume samples. The reported LOD for HACH® method 8149 is 0.007 mg L<sup>-1</sup>;<sup>18</sup> therefore, the concentrations of the filter spikes were  $0.007 \text{ mg L}^{-1}$ ,  $0.035 \text{ mg L}^{-1}$ , and  $0.070 \text{ mg L}^{-1}$ . The filters were extracted and analyzed according to the colorimetric method. Using the standard error of the regression and the slope of the response curve, while correcting for the dilution factors, the LOD was 5.2 µg filter<sup>-1</sup>. The limit of quantification (LOQ; 3.33 times the LOD<sup>19</sup>) was 17 μg filter<sup>-1</sup>. Under the standard conditions for filter collection (8 h at 2.0 L min<sup>-1</sup>), the loading of a filter at 0.1 times the TLV is 19 μg filter<sup>-1</sup>. Because the new method has a LOQ lower than 0.1 times the TLV of the most conservative work place exposure limit (ACGIH,  $0.2 \text{ mg m}^{-3}$ ), the method can satisfy analytical needs.

The accepted methods for determining the amount of manganese in airborne particulate matter<sup>16,17</sup> describe

**Table 1** Analysis of manganese(II) nitrate spikes on PVC filters at 0.1, 0.5, 1.0, and 2.0 times the TLV of 0.2 mg m $^{-3}$  using the colorimetric method<sup>a</sup>

| Spike quantity/<br>µg filter <sup>-1</sup> | $\begin{array}{l} Mean/\mu g \\ filter^{-1} \pm SD \end{array}$ | % Recovery | % RSD | % Bias |
|--|---|------------|-------|--------|
| 19   | $18.4 \pm 0.4$  | 97.1       | 2.3   | -2.9   |
| 95   | $96.7 \pm 2$  | 101.8      | 2.2   | 1.8    |
| 190  | $187 \pm 5$   | 98.4       | 2.6   | -1.6   |
| 380  | $389 \pm 4$   | 102.4      | 2.4   | 2.4    |

 $^{a}$  N=6 for all concentration levels. SD = standard deviation. RSD = relative standard deviation.

**Table 2** A comparison of manganese in welding fume produced from the ArcTec 41 and E11018-M electrodes collected by a multiport sampler measured using ISO Method 15202-2 or the colorimetric method<sup>a</sup>

| Electrode | $ISO \\ method/\\ \mu g \ filter^{-1} \pm SD$ | Colorimetric<br>method/<br>µg filter <sup>-1</sup> ± SD | Difference (%) <sup>b</sup> |
|-----------|---|---|-----------------------------|
| ArcTec 41 | 104 ± 6                                       | 105 ± 7   | 0.1                         |
|           | $186 \pm 5$                                   | $175 \pm 6$   | -5.9                        |
| E11018-M  | $18 \pm 1$                                    | $12 \pm 1$  | -33                         |
|           | $27 \pm 1$                                    | $21 \pm 2$  | -22                         |

a N = 4 for all sample groups. SD = standard deviation.
b Difference = [(colorimetric value - ISO value)/ ISO value] × 100.

collecting the aerosol on PVC or MCE filters, dissolving the aerosol using nitric and hydrochloric acids, and analyzing the resulting solution for total manganese with an ICP-OES. These methods were compared with the colorimetric method using a multiport sampler to collect air filter samples. Cassettes prepared for this study using the multiport sampler contained uniform loadings of manganese in the welding fume, as demonstrated by the results with the ISO method (RSD <3%, average manganese content =  $26.7 \mu g \text{ filter}^{-1}$ , N = 8). If the assumption is made that the filters in the eight cassettes were loaded with equivalent masses of manganese, the averages of the data produced by the different methods may be compared statistically.

The multiport sampler was used to collect fume while welding with ArcTec 41 electrodes (16% Mn). The number of electrodes used and the sample collection times were varied in order to obtain a variety of loading levels. Each set of eight cassettes was split into two groups: four were analyzed using the ISO method and four using the colorimetric method (Table 2). The means of the manganese masses measured with the colorimetric method are not statistically different (P > 0.05)from the means measured with the ISO method. Additional samples of fume were collected while welding with another type of electrode (E11018-M electrodes, <5% Mn). These fume samples were analyzed to evaluate the performance of the colorimetric method for analysis of fume containing lower concentrations of manganese and a different flux composition (Table 2). The amount of manganese measured is near the LOQ for the method; the results from the colorimetric method are statistically different (P < 0.05) from the manganese measured by the ISO method.

To evaluate the cause of the low recovery of the manganese in some samples, solutions produced from the dissolution of welding fume from both types of electrodes and both dissolution techniques were analyzed by ICP-OES (Table 3). The results illustrated that not all of the compounds that contain metals in the welding fume were dissolved by the acidic hydrogen peroxide extraction. The largest concentrations of ions other than manganese were iron and calcium. The color development of manganese(II) might have been impacted by the presence of iron, <sup>18</sup> so an interference study was conducted to evaluate the effect of elevated concentrations of iron(III) or iron(II) in the extraction solution. Duplicate spike solutions, equivalent to 4000 µg filter<sup>-1</sup> of either iron(II) or iron(III), and 190 μg filter<sup>-1</sup> manganese(II), were prepared. The average recovery of manganese was 99.6%. This indicated that elevated concentrations of iron in solution did not impact the color development of manganese with PAN.

To determine if time was a factor that impacted manganese recovery during the dissolution of the welding fume, samples were analyzed after the 2 h extraction period and also after 24 h using an ICP-OES and the colorimetric method (Table 4). The quantity of manganese measured in the fume from the ArcTec 41 electrode remained constant in the acidic hydrogen peroxide extraction solution; no additional time was required to dissolve the manganese compounds. The manganese measured by the acidic hydrogen peroxide extraction and the colorimetric method was equivalent to the amount of manganese measured by the ISO method (P > 0.05). The results produced from analysis of the acidic hydrogen peroxide extraction solution using an ICP-OES agreed with the manganese measured by the colorimetric method. The iron results revealed that approximately half of the iron was dissolved by the acidic hydrogen peroxide extraction when compared to the amount measured using the ISO method. The results for the E11018-M electrode show that the quantity of manganese measured by acidic hydrogen peroxide extraction and the colorimetric method increases slightly over 24 h. The results of the analysis of the acidic hydrogen peroxide extraction solution with ICP-OES also indicated that both the measured manganese and iron concentrations increase over time. The difference in the extraction efficiency appears to be correlated with the ratio of iron to manganese. In the ArcTec 41 electrode fume, the ratio of iron to manganese was approximately 1: 1 and the acidic hydrogen peroxide extraction dissolved the manganese compounds rapidly. As the ratio of iron to manganese in the fume

**Table 3** A comparison of metals measured by ICP-OES in replicates of welding fume collected with a multiport sampler dissolved using either the ISO Method 15202-2 or the acidic hydrogen peroxide extraction<sup>a</sup>

| Metal/ $\mu g \ filter^{-1} \pm SD$ | ArcTec 41 electrode |   | E11018-M electrode |   |
|-------------------------------------|---------------------|---|--------------------|---|
|                                     | ISO method          | Acidic H <sub>2</sub> O <sub>2</sub> <sup>b</sup> | ISO method         | Acidic H <sub>2</sub> O <sub>2</sub> <sup>b</sup> |
| Mn                                  | 178 ± 6             | 175 ± 8   | 26 ± 1             | 24 ± 2  |
| Fe                                  | $166 \pm 9$         | $84 \pm 7$  | $74 \pm 4$         | $69 \pm 6$  |
| Ca                                  | $21 \pm 5$          | <1  | $34 \pm 10$        | $22\pm2$  |
| Cr                                  | $8 \pm 0.7$         | $5\pm3$   | $0.3 \pm 0.2$      | $0.4 \pm 0.06$                                    |
| Cu                                  | $0.4 \pm 0.2$       | < 0.1   | $0.7 \pm 0.08$     | $0.3 \pm 0.03$                                    |
| Ni                                  | $18 \pm 0.9$        | $8.6 \pm 0.8$                                     | $2.5 \pm 0.4$      | $1.6 \pm 0.2$                                     |

**Table 4** A comparison of manganese and iron measured in welding fume collected with a multiport sampler using strong acid digestion followed by ICP-OES analysis (ISO Method 15202-2) or acidic hydrogen peroxide extraction followed by colorimetric method or ICP-OES analysis<sup>a</sup>

| Electrode | Extraction method/analysis method                               | Extraction time before analysis | $Mn/\mu g \ filter^{-1} \pm SD$ | $Fe/\mu g \ filter^{-1} \pm SD$ |
|-----------|---|---------------------------------|---------------------------------|---------------------------------|
| ArcTec 41 | Acidic H <sub>2</sub> O <sub>2</sub> /colorimetric <sup>b</sup> | 2 h                             | 175 ± 6                         |                                 |
|           | Acidic H <sub>2</sub> O <sub>2</sub> /colorimetric <sup>b</sup> | 24 h                            | $176 \pm 8$                     |                                 |
|           | Strong acid digestion/ICP-OES <sup>c</sup>                      | 0 h                             | $178 \pm 6$                     | $166 \pm 9$                     |
|           | Acidic H <sub>2</sub> O <sub>2</sub> /ICP-OES <sup>d</sup>      | 2 h                             | $175 \pm 8$                     | $84 \pm 7$                      |
| E11018-M  | Acidic H <sub>2</sub> O <sub>2</sub> /colorimetric <sup>b</sup> | 2 h                             | $13 \pm 2$                      |                                 |
|           | Acidic $H_2O_2$ /colorimetric <sup>b</sup>                      | 24 h                            | $16 \pm 0.4$                    |                                 |
|           | Strong acid digestion/ICP-OES <sup>b</sup>                      | 0 h                             | $14 \pm 0.4$                    | $41 \pm 1$                      |
|           | Acidic H <sub>2</sub> O <sub>2</sub> /ICP-OES <sup>d</sup>      | 2 h                             | $13 \pm 0.6$                    | $26 \pm 2$                      |
|           | Acidic H <sub>2</sub> O <sub>2</sub> /ICP-OES <sup>d</sup>      | 24 h                            | $15 \pm 0.4$                    | $38 \pm 1$                      |

<sup>a</sup> N = 4 for all sample groups. SD = standard deviation. <sup>b</sup> Filters extracted with acidic hydrogen peroxide solution and analyzed using the colorimetric method. <sup>c</sup> Filters dissolved with nitric and hydrochloric acids and analyzed by ICP-OES. <sup>d</sup> Filters extracted with acidic hydrogen peroxide solution and analyzed by ICP-OES.

increased (approximately 3:1 in the E11018-M electrode fume), the acidic hydrogen peroxide extraction required additional time to dissolve the manganese compounds. The data indicated that a portion of the manganese may have combined with iron in complex oxide structures, such as those described by Zimmer and Biswas.<sup>3</sup> No other metal concentrations that were included in the multielement analysis using an ICP-OES in the welding fume correlated with the increases in manganese concentrations over time.

Based upon the differences in manganese measured in the extraction solution after 24 h, an experiment was designed to determine the optimum length of time for dissolution of manganese into the acidic hydrogen peroxide extraction solution. Using the multiport sampler, additional sets of welding fumes were collected from the E11018-M and ArcTec 41 electrodes. The mass of welding fume collected from the E11018-M electrodes was increased to ensure the mass of manganese would be above the LOQ.

The amount of manganese on four of the filters from each type of electrode was measured following the ISO method. The amount of manganese on the four remaining filters from each type of electrode was measured after 2, 4, 8, 16, 24, and 48 h. At the end of each time interval an aliquot was removed from the extraction solution and analyzed using the colorimetric method. The manganese reported was calculated as the total manganese extracted after correction for solution volumes. For the fume from the ArcTec 41 electrodes, the average amount of manganese measured by the ISO method (293  $\pm 10 \text{ µg filter}^{-1}$ ) and the colorimetric method after a 2 h extraction period (290  $\pm$  27 µg filter<sup>-1</sup>), was equivalent (P > 0.05). For the fume from the E11018-M electrodes, the average amount of manganese measured by the ISO method  $(62 \pm 0.8 \,\mu g \, filter^{-1})$  and the colorimetric method after a 2 h extraction period (56  $\pm$  6  $\mu$ g filter<sup>-1</sup>) was statistically different (P < 0.05). After an 8 h extraction, the average amount of manganese measured by the colorimetric method (64  $\pm$  2  $\mu g$ filter<sup>-1</sup>) was equivalent to the ISO method (P > 0.05). This indicates that an extended extraction time may be required to recover the total amount of manganese when the iron to manganese ratio is high in the welding fume.

In conclusion, the results presented in this paper demonstrate that the new colorimetric method can be used to make quantitative measurements of manganese in welding fume.

The workplace air filter samples can be collected according to standard sampling methods. At the end of the work day, the welding fume samples can be extracted into an acidic hydrogen peroxide solution using sonication. Following the extraction, the samples can be analyzed using commercially available reagents on a spectrophotometer. If high amounts of iron are expected in the samples, the extraction time can be extended overnight and the samples analyzed the following day. The method can provide accurate and precise values when compared to values produced by the ISO method. Using sonication and the colorimetric method, measurements of manganese exposure in the workplace from aerosols can be made and reported to workers and managers within 24 h. This could prove to be a valuable tool for improving work practices and reducing exposure to manganese from welding fume.

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## References

- 1 J. M. Antonini, Crit. Rev. Toxicol., 2003, 33, 61-103.
- 2 W. Matczak and J. Gromiec, Appl. Occup. Environ. Hyg., 2002, 17, 296–303.
- 3 A. T. Zimmer and P. Biswas, *J. Aerosol Sci.*, 2001, **32**, 993–1008.
- 4 W. S. Beckett, in *Occupational and Environmental Respiratory Disease*, ed. P. Harber, M. B. Schenker and I. R. Balmes, Mosby-Year Book, St. Louis, 1996, pp. 70–714.
- B. S. Levy and W. J. Nassetta, *Int. J. Occup. Environ. Health*, 2003, 9, 153–163.
- 6 B. A. Racette, L. McGee-Minnich, S. M. Moerlein, J. W. Mink, T. O. Videen and J. S. Perlmutter, *Neurology*, 2001, 9, 8–13.
- 7 A. H. Sadek, R. Rauch and P. E. Schulz, Int. J. Toxicol., 2003, 22(5) 393-401
- 8 R. M. Park, R. M. Bowler, D. E. Eggerth, E. Diamond, K. J. Spencer, D. Smith and R. Gwiazda, *Neurotoxicology*, 2006, 27, 373–84.
- 9 R. Bast-Pettersen, D. G. Ellingsen, S. M. Hetland and Y. Thomassen, Int. Arch. Occup. Environ. Health, 2004, 77, 277–287.
- 10 C. M. Fored, J. P. Fryzek, L. Brandt, G. Nise, B. Sjogren, J. K. McLaughlin, W. J. Blot and A. Ekbom, J. Occup. Environ. Med., 2006, 63, 135–40.
- M. M. A. Boojar and F. Goodarzi, J. Occup. Environ. Med., 2002, 44, 282–290.

- 12 U. Buerke, J. Schneider, J. Rosler and H. J. Woitowitz, Am. J. Ind. Med., 2002, 41, 259–68.
- 13 J. M. Antonini, M. D. Taylor, A. T. Zimmer and J. R. Roberts, J. Toxicol. Environ. Health, 2004, 67, 233–49.
- 14 NIOSH Pocket Guide to Chemical Hazards, Department of Health and Human Services, Centers for Disease Control and Prevention, Publication No. 2005-149, Sept 2005, p. 191.
- 15 American Conference of Governmental Industrial Hygienists, Threshold Limit Values and Biological Exposure Indices, ACGIH, Cincinnati, Ohio, 2006.
- 16 NIOSH Manual of Analytical Methods, 4th edn, 1994, Cincinnati, OH, USA Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health.
- 17 International Organization for Standardization, ISO 15202-2-2001, Workplace Air—Determination of Metals and Metalloids in

- Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry—Part 2: Sample Preparation, Annex C: Sample Dissolution Using Nitric Acid and Hydrochloric Acid on a Hotplate, ISO, Geneva, Switzerland, 2001.
- 18 Hach Method 8149, 1-(2-pyridylazo)-2-napthol PAN Method, DR/2400 Spectrophotometer Procedure Manual, Hach Company, Loveland, CO, 2002.
- 19 E. R. Kennedy, T. J. Fischbach, R. Song, P. M. Eller and S. A. Shulman, *Guidelines for Air Sampling and Analytical Method Development and Evaluation*, (DHHS [NIOSH] Publ. No. 95-117), NIOSH, Cincinnati, OH, 1995.
- 20 F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, John Wiley & Sons, New York, 5th edn, 1988, pp. 702–708.
- 21 CRC Handbook of Chemistry and Physics, ed. R. C. Weast, CRC Press, West Palm Beach Florida, 58th edn, 1977–1978, p. D-142.