

# Welder Exposure to NO and NO<sub>2</sub> during Argon-Shielded Arc Welding on Aluminum Alloys

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# Abstract

**Objective:** This work was performed to assess welder exposure to NO and  $NO<sub>2</sub>$  and to assess the importance of these gases in the hierarchy of contaminants produced during welding (GMAW [MIG welding], GTAW [TIG welding], plasma cutting) on aluminum alloys.

Methods: Personal air samples in the breathing zone were collected on welders using a small, person-portable, direct-reading, datalogging instrument containing an electrochemical sensor rated for  $NO<sub>2</sub>$  and colorimetric detector tubes rated for NO to assess exposure during welding.

Results: Exceedance of the Threshold Limit Value -Time-Weighted Average (TLV-TWA) of 0.2 ppm (parts per million) averaged over 8 hours for  $NO<sub>2</sub>$  and the Ceiling Limit of 1 ppm used by some jurisdictions was likely during GTAW (TIG welding) in poorly ventilated conditions. Exceedance of these limits was unlikely during plasma arc cutting and GMAW (MIG welding). Exceedance of the TLV-TWA of 25 ppm for NO was unlikely to occur.

Conclusion: Exceedance of the TLV-TWA of 0.2 ppm and the Ceiling Limit of 1 ppm mandated in some jurisdictions for exposure to  $NO<sub>2</sub>$  during argon-shielded GTAW on aluminium alloys is likely to occur in the shipyard environment examined during this study. Exceedance of Exposure Limits for  $NO<sub>2</sub>$  during GMAW or plasma arc cutting is unlikely to occur. The critical substance at the top of the exposure hierarchy involving a complex mixture could be a gas. As well, this substance could be process-specific (GTAW versus GMAW). This situation illustrates the importance of monitoring worker exposure in consideration about the likelihood of exceedance of Exposure Limits and identification of critical substance(s) in the hierarchy of contaminants produced during a process.

Keywords: Aluminium alloys, Nitric oxide (NO), Nitrogen dioxide (NO<sub>2</sub>), Arc welding, GMAW (MIG welding), GTAW (TIG welding)

# Introduction

Arc welding and plasma cutting on aluminum alloys are common processes in the aluminum shipbuilding environment. Arc welding and plasma cutting produce a number of particulate and gaseous air contaminants of concern to human health. Gaseous contaminants include ozone  $(O_3)$ , nitric oxide (NO) and nitrogen dioxide  $(NO<sub>2</sub>)<sup>1</sup>$ . Nitric oxide results from reaction between nitrogen and oxygen on hot metal surfaces in the industrial environment<sup>2,3</sup>. Nitrogen dioxide results from subsequent reaction between nitric oxide and atmospheric oxygen or ozone.

This article is one of a series concerning the industrial hygiene aspects of arc welding on aluminium alloys<sup> $4-9$ </sup>. These articles reported on oxygen levels during arc welding, the possible role of argon in unusual fatigue in production welders, ultra-violet emissions and use of methanol as a coolant/lubricant during milling. Additional articles submitted for review but not yet referenced focus on selection of technology for measurement of nitric oxide and nitrogen dioxide and ozone and exposure to airborne particulates.

This document reports on determination of exposure of workers to  $NO$  and  $NO<sub>2</sub>$  during argon-shielded Gas Metal Arc Welding (GMAW) also known as MIG welding, Gas Tungsten Arc Welding (GTAW) also known at TIG welding and plasma cutting on aluminium alloys. The technical literature contains little information concerning exposure determination on welders to nitric oxide and nitrogen dioxide during arc welding on aluminum alloys. Factors influencing the relative level of each type of emission could reflect the type of welding

process as well as the quantity of heated metal.

NO and  $NO<sub>2</sub>$  are primarily irritants of membranes in the eyes, nose and respiratory system at levels normally encountered in workplaces<sup>10,11</sup>. NO is an upper respiratory tract irritant. NO also can cause hypoxia/cyanosis and formation of nitrosyl hemoglobin. In this situation, NO replaces oxygen in the binding site on the heme ring. NO<sub>2</sub> is a lower respiratory tract irritant. NO<sub>2</sub> is believed to be about 5 times more toxic than NO. Prolonged exposure to  $NO<sub>2</sub>$  at levels elevated above current regulatory limits can cause bronchitis and tightness of the chest.

Many workplace regulators have adopted the Threshold Limit Values (TLVs) published by the American Conference of Governmental Industrial Hygienists (ACGIH) as Exposure Limits to ensure worker protection against exposure to air contaminants such as NO and  $NO<sub>2</sub><sup>12</sup>$ . TLVs are airborne concentrations to which it is believed that nearly all workers may be repeatedly exposed without adverse health effects. TLVs are based on consideration about protection from impairment of health, reasonable freedom from irritation, narcotic effects, nuisance, other forms of stress, and short- and long-term effects on internal organs and systems. The basis for the TLV varies with the substance. ACGIH indicates that TLVs are guidelines not fine lines between safe and unsafe conditions. TLVs include safety factors. The purpose for the safety factor is to ensure protection of nearly all workers following repeated daily exposure at the level of the TLV. When adopted by governments as regulatory limits, TLVs become speed limits and acquire the full meaning of the term $^{13}$ .

The current TLV-TWA(Time-Weighted Average) for NO is 25 ppm and 0.2 ppm for  $NO_2$ , respectively<sup>12</sup> (ppm is parts per million, a unit of concentration). TLV-TWAs are the average concentration over the workshift of 8 hours. This study examined exposure to  $NO<sub>2</sub>$  in a jurisdiction that uses a Ceiling Limit of 1  $ppm<sup>13</sup>$ . A Ceiling Limit is a concentration not to be exceeded during the workday. A Ceiling Limit demands detection technology that can respond rapidly to change in conditions and the ability to store measured levels during short intervals in the work shift.

The value of Exposure Limits is not constant over time. To illustrate, the TLV for  $NO<sub>2</sub>$  decreased in 2011 from a TWA of 3 ppm to a TWA of  $0.2$  ppm $^{10,11}$ . This decrease has a huge potential impact on the overall importance of  $NO<sub>2</sub>$  as a contaminant to which welders are exposed. With this massive change, what was acceptable one day as an exposure could become a serious overexposure the day following. Many TLVs have decreased over the years. Each decrease in the Exposure Limit of one substance in a complex mixture could change the relationship with other substances in the

exposure hierarchy. The only way to ascertain the impact *a priori* of a decrease in an Exposure Limit is to have a comprehensive database created through extensive and thorough air sampling.

The preceding discussion highlights one of the most important strategic concepts in the practice of industrial/occupational hygiene: the critical contaminant. The critical contaminant controls the response necessitated by occupational health and safety regulations. Typically, in any process, one air contaminant will dominate assessment of exposure and the need to implement control methods. This contaminant is not necessarily obvious by inspection of reference documents. Identification often requires air and sometimes other types of sampling. Once identification of the critical contaminant occurs, surveillance of exposure and control efforts can focus on that substance. This is especially important when exceedance of the Exposure Limit can occur.

Welding is more complex than other processes because of the generation of many air contaminants including both gaseous and particulate substances<sup>1</sup>. Dominance reflects the interaction between the concentration in air and the Exposure Limit. Exposure Limit as used here includes all limits adopted for controlling workplace exposure as used by regulators. Concentration of airborne contaminants during arc welding is the outcome of interaction of many factors. These reflect the process, composition of the base metal and filler, the surface of the base metal(polished versus unpolished, coated versus uncoated, plated versus unplated), the geometric relationship between the source of the contamination (the arc) and the posture and orientation of the torso of the welder, and duration of exposure. The combination of low occurrence of an element in the metal combined with a low Exposure Limit does not necessarily ensure against dominance of the situation. Dominance controlling the need for control measures in a series of alloys could be alloy-specific.

Recent effort in the area of industrial/occupational hygiene has stressed the importance of statistics and modelling in characterizing workplace exposures such as those occurring during arc welding<sup>14,15</sup>. A statistical approach potentially has the ability to accommodate differences in style of welding, and changes in geometric relationships, duration of work and other factors that can influence exposure. Sufficient data collection through air sampling provides the basis for predicting relationships in the exposure hierarchy. Comparison of statistically determined values against the Exposure Limit provides the basis for determining whether an element in the alloy or a gas such as ozone,  $NO$  or  $NO<sub>2</sub>$ could exceed the current Exposure Limit and by how much. The substance exceeding the Exposure Limit most consistently and by the greatest demonstrable

amount occupies the position at the peak of the hierarchy and will dictate the response needed to achieve compliance.

Another consideration in the determination of controlling substance is the type of respiratory protection approved by NIOSH (US National Institute for Occupational Safety and Health) $16,17$ . Generally, a filtering or sorbent cartridge+appropriate facepiece is sufficient to provide protection against exposure to airborne particulates produced during welding18,19. This was the case for CrVI in a welding plume during argon-shielded arc welding on aluminum alloys<sup>8</sup>. Obtaining sufficient CrVI for analysis under real-world conditions necessitated long-duration welding utilizing a mechanized welding unit. The analytical procedure determines conversion of elemental Cr in the alloy to CrIII and CrVI in the plume.

Use of a sorbent cartridge is not necessarily possible in situations where exposure to gaseous substances is occurring. To illustrate, a supplied-air respirator is required for protection against low level of oxygen and against levels of  $NO$ ,  $NO<sub>2</sub>$  and ozone that exceed the respective Exposure Limits<sup>16,17</sup>.

McManus and Haddad $6.7$  explored this question concerning the level of oxygen and by extension, the level of argon experienced by welders and other workers through extensive air sampling during argon-shielded welding on aluminum alloys. These authors determined in minute-by-minute air sampling during production welding that in only six out of 14,500 measurements obtained in various situations and geometries did the level of oxygen decrease below 19.5% (the Exposure Limit in most jurisdictions). The lowest value, 17.6%, persisted less than one minute and recovered immediately afterward as shown in the successive measurement. This investigation demonstrated the essential importance of a datalogger in situations where a Ceiling Limit (or in this case a trough) was involved. The instrument used in this study was very compact and contained an internal pump. The instrument was positioned in the upper pocket of the coveralls of the welder. Only the probe was exposed to damage from the welding environment.

A companion to this investigation compared the response of a group of handheld, portable datalogging instruments containing electrochemical sensors rated for  $NO<sub>2</sub>$  to an  $NO<sub>2</sub>$ -specific air pollution analyzer during simultaneous exposure to samples of welding plumes collected during argon-shielded welding on aluminum alloys [submitted for publication, not yet referenced]. This study showed the suitability of these instruments for assessing exposure to  $NO<sub>2</sub>$  during arc welding of aluminum alloys despite the potential for cross-reaction due to interfering substances. Given that the Exposure Limit for  $NO<sub>2</sub>$  now is extremely small, specificity and absence of cross-reaction are extremely important.

 The most accurate assessment of exposure occurs when the sensitive element of the measuring device is positioned in the breathing zone of the worker. The breathing zone is an imaginary sphere having a radius about 0.6 m centered in the middle of the head. This sphere encloses the region in space from which the body receives air during inhalation $2<sup>0</sup>$ . A further complication to sampling in the welding environment is an important function of the welding helmet that is not often recognized. The welding helmet acts as a barrier to deflect the welding plume away from the face. The welding helmet prevents the plume from making contact with the inlet openings of the respiratory system, namely the nostrils and the mouth. Research involving welders during working in a locomotive manufacturing operation showed that the concentration of contaminants outside the welding helmet is about 1.4 times the level inside<sup>21</sup>. Results obtained by Liu *et al*. in a similar study indicated a factor of  $1.1^{22}$ . These differences are not surprising given the unpredictability of movement of the head, torso, and welding helmet in time and space.

Assessment of exposure to airborne contaminants during welding is technically challenging even with small, portable instruments. This situation arises for several reasons. First is the need to ensure that the welder is protected properly against welding hazards. The welding helmet is an integral part of this protection. The welding helmet must fit as designed around the face and neck and not be forced partly open in order to accommodate the measuring equipment. The necessity to position the sampling instrument to obtain a sample representative of exposure must not compromise protection provided by welding protective equipment.

The second reason results from the design of these instruments. Few instruments are designed to sample effectively in the challenging and potentially destructive environment created during welding. There are two fundamental design options regarding sensor position in compact, hand-held instruments. The first option positions the sensor on the external surface of the instrument. Obtaining the sample requires exposure of the surface of the instrument and the sensor to the rigors of the environment including the hazards for which the worker is receiving protection from the welding helmet. This placement puts the instrument and the sensor highly at risk from damage. Portable instruments positioned in the breathing zone of the welder can interfere with and compromise the protective function of the welding helmet.

The second option in instrument design is to bring the sample to the sensor. This choice uses an internal or compact external pump and a sampling probe able to be positioned in the breathing zone remote from the body of the instrument. The pump provides the ability to position the intake of the sampler in the breathing zone without hindrance in use of welding protective equipment and protects the instrument against physical damage. An add-on, external pump adds to the volume of the instrument. This creates difficulty in positioning the instrument in the pocket of a pair of coveralls.

An additional useful feature in some of these devices is an internal datalogger. The datalogger can provide a minute-by-minute record of the exposure profile. This record is invaluable for identifying, investigating, and quantifying unexpected conditions in the environment in which work is occurring. Datalogging can assist in detection of additional substances not anticipated in the assessment of the environment. A datalogger also is essential for assessing compliance with requirements of a Ceiling Exposure Limit for  $NO<sub>2</sub>$ .

Measurement of nitric oxide also occurred during this work. Measurement of NO is a low priority because the TLV-TWA of 25 ppm is considerably higher than the TLV-TWA for  $NO<sub>2</sub>$ . As well, NO levels measured using an air pollution instrument described in previous work usually were less than 1 ppm and usually exceeded the  $NO<sub>2</sub>$  levels only by a factor of five [submitted for publication, not yet referenced]. Since there is a one-toone correspondence between molecules of  $NO<sub>2</sub>$  created and molecules of NO destroyed, there is little likelihood of exceeding the TLV-TWA for nitric oxide<sup>10,11</sup>.

This work occurred at a shipyard located in Vancouver, British Columbia, Canada during fabrication of ship structures from aluminum alloys by GMAW and GTAW (MIG and TIG welding processes). Structures created during fabrication have geometric configurations ranging from simple to complex. Welding occurred under open, partially enclosed, semi-enclosed, and completely enclosed conditions. The hull portion of the vessel was fabricated using Pechiney Rhenalu 5383-H321 plate (thickness ranging from 6 mm to 25 mm). The extrusion materials were  $6082$ -T6 and  $6061$ -T6 alloys<sup>23</sup>. Fabrication of the hull was occurring during this investigation. The 5083 alloy with thickness as little as 2.5 mm was utilized in areas throughout the vessel other than the hull. Primary welding equipment used on this project was the ESAB SVI 450 CV/CC (ESAB Canada, Mississauga, ON) power source with the MIG 4HD ultra pulse wire feeder and a push/pull gun operated in the pulsed GMAW mode. The ESAB-A2 tractor and CV/CC 652 power source were used on flat groove welds throughout the project. Table 1 describes welding conditions. The shield gas used during this work was argon. Welding activity met requirements of CAN/  $CSA W47.2^{24}$ .

#### **Results**

Table 2 presents results from sampling for  $NO<sub>2</sub>$  using the AIM 4501 during GMAW (MIG welding), plasma arc cutting, and GTAW(TIG welding). Table 2 includes ASME (American Society of Mechanical Engineers terminology for welding orientation<sup>25</sup>. The workers wore the instrument for most of the shift, generally 6 to 7 hours. Exposures were intermittent and infrequent. Intermittency and infrequency depend on the type of work and are characteristic of welding. The focus of this investigation was exceedance relative to the Ceiling Limit of 1 ppm enforced by WorkSafeBC and not calculation of a time-weighted average<sup>13</sup>. For this reason, Table 2 provides the minimum of detail regarding individual readings.

Most readings for  $NO<sub>2</sub>$  obtained during argon-shielded, GMAW were 0.0 ppm. Those that were detectable occurred in isolated clusters and ranged from 0.1 ppm to 0.4 ppm. Conditions during the work in which these readings were measured were highly confining. Conditions that are highly confining are conducive to stagnation and aging of the plume. Reaction involving NO and ozone or oxygen to form  $NO<sub>2</sub>$  occurs under conditions of stagnation and aging. Results obtained here strongly suggested that nitrogen dioxide levels would not exceed the TLV-TWA of 0.2 ppm or the Ceiling Limit of 1 ppm during argon-shielded GWAW.

All but one of the readings obtained for  $NO<sub>2</sub>$  during

**Table 1.** Welding parameters during sampling for  $NO<sub>2</sub>$ .

Current amperes	Voltage volts
190 to 240	24 to 25
160 to 190	24 to 25
180 to 220	24 to 25

Current shall not vary more than  $\pm 15\%$ .

Voltage shall not vary more than  $\pm 10\%$ .

When using 6061 base material, current and voltage are higher.

CSA-CWB W47.2 Aluminum was followed during this work<sup>24</sup>.

Table 2. Nitrogen dioxide levels-long duration samples (Instrumental).



Each entry reports on an independent 6 to 7 hour sample.

The emphasis of these reports was comparison to compliance with a Ceiling Limit and not calculation of a time-weighted average.

\*This description reflects nomenclature for welding positions<sup>25</sup>.

plasma arc cutting were 0.0 ppm. The sole detected reading of  $NO<sub>2</sub>$  of 0.1 ppm was half of the TLV-TWA of 0.2 ppm and low compared to the Ceiling Limit of 1 ppm. Nitrogen oxides are a possible product of plasma arc cutting. Plasma arc cutting occurred on a table containing a downdraft exhaust hood. Results obtained here coupled with visual observation of the operation of this equipment suggest that the exhaust system was highly effective in collecting the plume. Faulty collection was readily apparent from emission of a considerable plume above the plane of the table.

Most of the readings obtained for  $NO<sub>2</sub>$  during argonshielded GTAW were  $0.0$  ppm. When detected,  $NO<sub>2</sub>$  levels occurred in isolated clusters and ranged from 0.1 ppm to 5.8 ppm. These values ranged from half to very high compared to the TLV-TWA of 0.2 ppm and the Ceiling Limit of 1 ppm. Some of these readings exceeded the Excursion Limit of 5 times the value the TLV-TWA of 1.0 ppm<sup>12,13</sup>. These values are high enough to indicate that compliance with the requirements of the Ceiling Limit of 1 ppm and possibly the TLV-TWA of 0.2 ppm without the use of control measures is not possible.  $NO<sub>2</sub>$  produced during GTAW on aluminum alloys is a possible critical contaminant in this process.

Table 3 presents results from short-duration sampling during welding activity using colorimetric detector tubes for NO. NO was detectable during air sampling using the colorimetric detector tubes only when GTAW was occurring. Results presented in Table 2 and Table 3 from both types of tests are complimentary since the NO is the source of the  $NO<sub>2</sub>$ . However, results provided by the instrument, in Table 2, are considerably more detailed because of datalogging capability. NO was undetectable in samples obtained during argon-shielded GMAW. Levels of NO detected during GTAW were low compared to the TLV-TWA of 25 ppm. Exceedance of the TLV-TWA was unlikely to occur.

## **Discussion**

The datalogger in the AIM 4501 retained a minuteby-minute record of conditions. Each retained value is the maximum from the 30 records obtained during each one-minute period. The ability to gain access to these values from a multi-hour exposure illustrates the value of instruments containing dataloggers in situations involving intermittent exposures of unknown duration





Each entry reports on an independent sample.

The emphasis of these reports was comparison to compliance with a Ceiling Limit and not calculation of a time-weighted average.

\*This description reflects nomenclature for welding positions25.

and magnitude during a workshift. The summary format used in Table 2 provides the best overview to understand the meaning of the data over the duration of the sample period.

The lapel-balaclava/bib combination likely does not receive the highest concentration of  $NO<sub>2</sub>$  that is measurable. Higher concentrations likely would be measured at locations on the front and side of the welding helmet, since the welder often positions the welding helmet in the path of the plume<sup>21,22</sup>. The important consideration is what the welder breathes behind the welding helmet in the absence of a respirator. A welder always will use face protection (a welding helmet), but not necessarily a respirator.

Interpretation of the Ceiling concept is an important part of discussion regarding implementation of these results. The real-world as well as the regulatory interpretation of the Ceiling concept has received no discussion in current literature. The Ceiling concept usually is enunciated as a concentration not to be exceeded at any time during the workshift<sup>12</sup>. Forty-eight of the current TLVs carry the Ceiling designation.

Part of the issue of real-world implementation of the Ceiling concept, as compared to the abstract definition, mentioned above, derives from limitations of measurement techniques. Concentrations measured for comparison against Ceiling Limits often are short-duration timeweighted averages (Time-Weighted Average refers to the usage of the concept by ACGIH as an 8-hour average). Requirements and limitations of the measurement technique define the duration during which the averaging of concentration occurs.

At the time the Ceiling concept was enunciated, the most rapid technique for assessing concentration was the colorimetric detector tube. These tubes were (and still are) the only technology available for assessing many of the substances to which the Ceiling designation applies. For substances for which detector tubes were not available, collection over considerably longer periods was required. This situation applies today, except that multiple techniques of measurement are available for some substances. These techniques sometimes include real-time, portable instruments, as used here.

As an example of this type of equipment, the AIM 4501 measures concentration every 2 seconds and records the maximum every minute. The Gastec colorimetric detector tubes used here provide a one- or twominute or longer time-weighted average, depending on the number of pump strokes and the duration per stroke. The Gastec piston pump pulls air rapidly during the initial draw and hence biases the result high when premature termination occurs. This means that the pump must complete the entire cycle while welding is occurring in order for the sample to be valid. In addition, in order to capture the magnitude of the exposure, sampling must occur within the period during which emission is occurring. Without following a welder during the entire day, the potential for capturing the magnitude and duration of exposure through use of detector tubes is small.

Measurement using other techniques such as sorbent tubes or bag collection followed by lab analysis provides only an average concentration that depends on the

When several techniques for measuring the same substance are available, the ability to obtain the same values depends on the stability of the concentration during the period of measurement. In the rapidly varying conditions that exist in a welding environment, the technique that provides the greatest resolution is most likely to record the highest concentrations and greatest exceedances. While this may be desirable from the perspective of accuracy and precision, this introduces considerable confusion with regard to assessing compliance with the Ceiling Limit.

The philosophy of interpretation of the Ceiling concept governs a cascade of events that can determine the survivability of entire industrial sectors. An extremely conservative view is that work for the day should stop on detection of an alarm based on the Ceiling Limit. A more lenient and pragmatic view is that work stops on detection of an alarm and can continue once correction of the cause has occurred. Responding to exceedances identified through the sounding of an alarm by an instrument is difficult. Ship structures are complex and often partly or completely enclosed. Ventilation to reduce the exposure must simultaneously preserve the integrity of the gaseous shield that surrounds the arc.

Preventing exceedance of regulatory limits that are very small in magnitude or instantaneous in application is extremely difficult. Observation and experience have shown that local exhaust ventilation systems are impractical and impracticable in the shipyard environment involving aluminum alloys where configurations are ever-changing. Aluminum is a nonferrous metal and not amenable to attachment of ventilation hoods using magnets. Clamping is not a practical method of attachment because of inconvenient geometry. The shipyard in this investigation addressed this situation by utilizing portable fans with and without attached duct, and employed an individual full-time to position them in various orientations in an attempt to ventilate the structures and to remove contamination.

Successful use of ventilation in exposure control where gas-shielding is employed is a study in conflict. Regulators mandate Exposure Limits as discussed here and use of ventilation as the primary means for achieving control. Welders function through the mandate of weld quality. Maintaining the gaseous shield around the area of the arc is the overriding concern of the welder. These requirements are mutually conflicting and difficult and often impossible to satisfy simultaneously.

Complicating matters further is the lack of a NIOSHapproved respirator cartridge for use against NO and

 $NO<sub>2</sub><sup>16,17</sup>$ . NIOSH tests and approves respiratory protection in the US. Should exceedance of the regulatory limit for  $NO<sub>2</sub>$  occur routinely, the only option for respiratory protection is the air-supplied respirator/welding helmet given the difficulties with ventilation discussed in this report. Entanglement of hoses used with air-supplied respirators is a serious issue in the shipyard environment where many welders are working simultaneously.

The situation examined in this study is highly complex. Exposures are short in duration, infrequent and unpredictable in occurrence. The process followed here for interpreting the meaning of these results attempts to resolve the significance and consequence of exceedance of the TLV-TWA and the Ceiling Limit.

## Conclusion

Exceedance of the TLV-TWA of 0.2 ppm and the Ceiling Limit of 1 ppm mandated in some jurisdictions for exposure to  $NO<sub>2</sub>$  during argon-shielded GTAW on aluminium alloys is likely to occur in the shipyard environment examined during this study. Exceedance of regulatory limits during GMAW or plasma arc cutting is unlikely to occur. The results obtained in this assessment show that the critical substance at the top of the exposure hierarchy that determines measures needed to achieve compliance with regulatory requirements involving a complex mixture could be a gas. As well, this substance could be process-specific. This situation illustrates the importance of monitoring worker exposure in consideration about the likelihood of exceedance of Exposure Limits and identification of critical substance(s) in the hierarchy of contaminants produced during a process.

## Materials and Methods

#### Measurement of  $NO<sub>2</sub>$

 $NO<sub>2</sub>$  was measured using the AIM 4501 (IST-AIM Corp., Richmond, BC). The instrument was calibrated according to recommendations from the manufacturer. This instrument contains a built-in sampling pump and a datalogger. The datalogger provided a minute-by-minute record of the concentration of  $NO<sub>2</sub>$ . The instrument was positioned into the pocket of the coveralls conveniently for the comfort of the wearer during work activity. The sampling probe was positioned on the front lapel or front edge of the balaclava or bib worn by the welder (Figure 1). This location is close to the source of air that is drawn into the gap between the welding helmet and the face for breathing. The lapel-balaclava/



Figure 1. Instrument Containing an Internal Pump and External Sampling Probe. The sampling probe is positioned in the breathing zone under the welding helmet. In this position, the sampling probe does not disturb the protective aerodynamics created by the welding helmet. The welding helmet must remain fully lowered against the torso in order to protect the head and face of the welder.

bib combination also is the position closest to the face that is common to the types of respiratory and other welding-related protection worn during this work. The intent in choosing the location on the lapel-balaclava/ bib combination was to ensure that the sample represented at least what was presented to the nose and mouth under the welding helmet without compromising welder safety.

#### Measurement of NO

Short-duration measurement of NO was obtained using colorimetric detector tubes (Gastec Corporation, Kanagawa, Japan, No.10, Nitric Oxide) in the over-theshoulder position. This product measures  $NO$  and  $NO<sub>2</sub>$ simultaneously using a two tubes connected in series $26$ . The first tube measures  $NO<sub>2</sub>$  in the incoming air. The second tube converts the NO to  $NO<sub>2</sub>$  and then uses the

same chemistry to measure the newly formed  $NO<sub>2</sub>$ . The minimum scale reading on the  $NO<sub>2</sub>$  tube is 2.5 ppm and 5 ppm for the NO tube. With the decrease of the TLV for  $NO<sub>2</sub>$  from 3 ppm to 0.2 ppm in 2011, the  $NO<sub>2</sub>$  tube was unable to respond appropriately to levels below the TLV in jurisdictions using the TLV as the Exposure  $Limit<sup>12</sup>$ . The jurisdiction in which this study occurred (Province of British Columbia, Canada) uses a Ceiling of 1 ppm, still too low for use of the colorimetric detector tube produced by Gastec<sup>13,26</sup>. Hence, readings from the  $NO<sub>2</sub>$  tube are not reported here. The short-duration samples were obtained only during exposure of the welder to the plume. Hence, these results represent the concentrations present only during exposure to the plume and not a combination of start-up and shutdown, welding activity, and related work not involving exposure to background conditions.

#### Statistical Calculations

Statistical calculations were performed using IHData-Analyst Lite Version 1.29 (Exposure Assessment Solutions, Inc., Morgantown, WV, [www.OESH.com\)](http://www.OESH.com).

#### Knowledgeable Consent

WorkSafeBC, the regulator in British Columbia, requires employers to assess the conditions of work. The assessment reported here required cooperation and active participation from welders and other workers at the shipyard. Everyone who participated was a volunteer and gave informed consent. Prior to the start, each prospective participant received a brief explanation about what the monitoring system did and what information it created and stored. Anyone uncomfortable with participation was excused, no questions asked, and without repercussion. No names were recorded to ensure that there was no means to identify participants.

This work involved about 20 production welders, 5 tackers and 5 fitters, the laborer who managed portable ventilation equipment, and two supervisors. Individual participation varied considerably from one session to multiple sessions depending on comfort in wearing the sampling equipment, interest in the project, and the type of work that was occurring. Monitoring attempted to obtain samples from all relevant types of activity. Sampling was spread among the group of workers over the duration of the sample period which occurred over several weeks. Sampling was dictated in part by availability of work in specific structures and different geometric configurations as indicated in the Table 2 and Table 3 in the Results. The realities intrinsic to this situation introduced considerable randomness because the schedule of work was not known in advance of seeking volunteers for a particular day. Driving sample col-

lection was the need to obtain as many samples as possible within the limited time available and a schedule that changed from day to day.

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# Conflict of Interest

The authors declare that they have no conflicts of interest with the contents of this article.

#### References

- 1. NIOSH (National Institute for Occupational Health and Safety). *Criteria for a Recommended Standard, Welding, Brazing, and Thermal Cutting* (DHHS (NIOSH) Publication No. 88-110), https://www.cdc.gov/niosh/ docs/88-110a/pdfs/88-110A.pdf(1988).
- 2. Seinfeld, J. H. in *Air Pollution: Physical and Chemical Fundamentals*(McGraw-Hill Inc., USA, 1975).
- 3. Perkins, H. C. in *Air Pollution* (McGraw-Hill Inc., USA, 1974).
- 4. McManus, T. N. & Haddad, A. N. UV and Blue Light Exposures in an Aluminum Shipbuilding Environment. *Int. J. Open Sci. Res*. **1**, 15-27 (2013).
- 5. McManus, T. N. & Haddad, A. N. Use of Methanol as a Coolant during Machining of Aluminum in a Shipbuilding Environment: A Failure to Assess and Manage risk. *Adv. Mat. Res*. **955-959**, 1061-1064 (2014).
- 6. McManus, N. & Haddad, A. N. Oxygen Levels during Welding Assessment in an Aluminum Shipbuilding Environment. *Prof. Safety* **60**, 26-32 (2015).
- 7. McManus, N. & Haddad, A. N. Argon-related Fatigue: An Investigation in an Aluminum Shipbuilding Environment. *Prof. Safety* **60**, 47-55 (2015).
- 8. McManus, T. N. & Haddad, A. N. Chromium Emissions during Welding in an Aluminum Shipbuilding Environment. *Weld. J*. **95**, 86-92 (2016).
- 9. McManus, T. N. & Haddad, A. N. Ozone: a critical contaminant produced during gas metal arc welding (GMAW) on aluminum alloys—resolving the shortversus long-duration sampling discrepancy. *Air Qual. Atm. Health* **Online First**, doi: 10.1007/s11869-018-

0634-9 (2018).

- 10. ACGIH (American Conference of Governmental Industrial Hygienists). in *Documentation of the TLVs and BEIs; Nitric Oxide* (American Conference of Governmental Industrial Hygienists, USA, 2001).
- 11. ACGIH (American Conference of Governmental Industrial Hygienists). in *Documentation of the TLVs and BEIs; Nitrogen dioxide* (American Conference of Governmental Industrial Hygienists, USA, 2001).
- 12. ACGIH (American Conference of Governmental Industrial Hygienists). in *TLVs and BEIs for Chemical Substances and Physical Agents & Biological Exposure Indices*(American Conference of Governmental Industrial Hygienists, USA, 2014).
- 13. WorkSafeBC. Occupational Health & Safety Regulation, Part 5, Chemical Agents and Biological Agents(BC Regulation 296/97, as amended), http://www2.worksafebc.com/publications/OHSRegulation/Introduction. asp#AboutOccupationalHealthSafetyRegulation (2018).
- 14. AIHA(American Industrial Hygiene Association). in *A Strategy for Assessing and Managing Occupational Exposures*, 4th edn (eds Jahn, S. D., Bullock, W. H. & Ignacio, J. S.) 361-453 (American Industrial Hygiene Association, Falls Church, VA, 2015).
- 15. AIHA (American Industrial Hygiene Association). *Mathematical Models for Estimating Occupational Exposure to Chemicals*, 2nd edn (eds Keil, C. B., Simmons, C. E. & Anthony, T. R.) 337-347 (American Industrial Hygiene Association, Fairfax, VA, 2009).
- 16. Bollinger, N. NIOSH Respirator Selection Logic (DHHS (NIOSH) Publication No. 2005-100), http:// www.aresok.org/npg/nioshdbs/docs/2005-100/chapter6.html(2004).
- 17. NIOSH (National Institute for Occupational Safety and Health). NIOSH Pocket Guide to Chemical Hazards (DHHS (NIOSH) Publication No. 2005-149), https:// www.cdc.gov/niosh/docs/2005-149/pdfs/2005-149.pdf (2007).
- 18. AIHA (American Industrial Hygiene Association). in *Respiratory Protection, a Manual and Guideline* (American Industrial Hygiene Association, Fairfax, USA, 2001).
- 19. 3M Occupational Health and Environmental Safety Division. in *2010 Respirator Selection Guide* (Minnesota Mining and Manufacturing, St. Paul, MN, 2010).
- 20. Lynch, J. R. in *Patty's Industrial Hygiene and Toxicology*, 3rd edn (eds Harris, R. L., Cralley, L. J. & Cralley, L. V.) 27-80 (John Wiley & Sons, Inc., USA, 1994).
- 21. Goller, J. W. & Paik, N. W. A Comparison of Iron oxide Fume Inside and Outside of Welding Helmets. *Am. Indust. Hyg. Assoc. J*. **46**, 89-93 (1985).
- 22. Liu, D., Wog, H., Quinlan, P. & Blanc, P. D. Welding Helmet Airborne Fume Concentrations Compared to Personal Breathing Zone Sampling. *Am. Indust. Hyg. Assoc. J*. **46**, 280-283 (1995).
- 23. Swint, W. ESAB's partnership with Canada's west coast shipbuilding industry. Pacificat 1000 series high speed

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ferry. *Svetsaren* **54**, 28-30 (2000).

- 24. CSA Group. Certification of Companies for Fusion Welding of Aluminum (CAN/CSA W47.2-11), https:// www.cwbgroup.org/certification-and-qualification/csaw472-fusion-welding-aluminum-company-certification (2011).
- 25. ASME (American Society of Mechanical Engineers).

in *2010 ASME Boiler and Pressure Vessel Code. IX Qualification Standard for Welding and Brazing Procedures, Welders, Brazers, and Welding and Brazing Operators*(American Society of Mechanical Engineers, USA, 2010).

26. Gastec. in Gastec Environmental Analysis Technology Handbook (Gastec Corporation, Japan, 2012).