"Improving Welding Toxic Metal Emission Estimates in California"

Final Report

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EXECUTIVE SUMMARY

An experimental effort was undertaken to expand and update Cr(VI) emission factors for stainless steel welding and included four welding processes: gas-metal arc welding (GMAW), shielded metal arc welding (SMAW), flux-core arc welding (FCAW) and pulsed gas-metal arc welding (P-GMAW). An enclosure was designed to permit isokinetic collection of total and PM 2.5 mass emission rates. The UCD enclosure compared favorably with the Standard American Welding Society (AWS) hood. A borate buffer modification to a standard colorimetric method for determination of Cr(VI) was evaluated, determined to be suitable for sample storage for periods up to at least three days, and permitted use of a commercial flow injection analysis (FIA) instrument, without bubble formation in its detector.

The emission factors for Cr(VI) from stainless steel electrodes were determined and compared to existing EPA data. The present results are of comparable magnitude to the EPA emission factors and those reported by an industry group under similar "average" conditions, typically within a factor of 2. Tests run without shielding gas for SMAW and FCAW produced an order of magnitude greater Cr(VI) emission per unit of electrode consumed.

The possible presence of vapor phase chromium was checked for using a modified Cal EPA Method 425 impinger train. The resulting estimate of Cr(VI) in the vapor phase was less than three percent of the solid phase Cr(VI) for all samples based upon detection limits of the assay, and therefore any gas phase Cr(VI) would be less than that amount. We conclude that the gas phase Cr(VI) is negligible for the purposes of an emissions inventory, and it is probable that there was no gas-phase Cr(VI) present in the cooled fumes.

The fraction of particles greater than 2.5 microns aerodynamic diameter was measured in a subset of samples using an IMPROVE sampler. The fraction greater than PM 2.5 ranged from 20 to 60%. The surprisingly large coarse fraction likely reflects the extremely rapid coagulation of primary aerosol particles because of their high concentration in the region of the arc and the greater density of the metallic particles.

The formation of Cr(VI) from standard electrode wires used for welding mild steel was below detection limit after removing an artifact in the analytical method. We believe that some residual particles from the ultrasonic extraction of the filters, after passage through a nominal 0.45 μm filter, resulted in a weak light scattering signal in the detector. After a second filtration through nominal 0.22 μm filters, the signal was reduced and after a second filtration through a 0.02 μm filter, the apparent Cr(VI) signal was reduced to the detection limit. Therefore the Cr(VI) emission factor reported for standard mild steel electrodes is presented as less than the detection limit. One cannot conclude that Cr(VI) will not be formed from mild steel electrodes. The amount depends upon the impurity level of Cr(VI) in the electrode. For the mild steel electrode type used to compare the AWS and UCD enclosures, the Cr-content was determined to be 0.012%.

RECOMMENDATIONS

Because of the large number of variables that potentially impact Cr(VI) emissions and the seeming impracticality of determining values of those variables for an emissions inventory, we recommend use of the average emission factors reported under test conditions that produce good weld quality. Those values should be accepted with an understanding that there will be an uncertainty of about a factor of two about the mean.

The Cr-content of many welding rods used for mild steel is not specified since the presence of Cr is because it is an impurity rather than deliberate addition. In order to improve the estimate of Cr(VI) for emissions for welding rods made of fused or mild steel it may be desirable to obtain analyses of Cr-content for a statistical sample of widely used commercial rods from different manufacturers. A rational basis for an estimate of the Cr(VI) emissions would be to assume that the same fraction of elemental Cr in the rod is converted to Cr(VI) and emitted as for stainless steel welding electrodes that have been tested using the same welding method, e.g., GMAW, FCAW, p-GMAW.

Recent studies completed after the experimental phase of this project had ended (Dennis et al, 2002) have illustrated that substantial reduction of Cr(VI) formation can be achieved by choice of shield gas composition and welding electrode additives. If the emissions inventory continues to demonstrate that Cr(VI) from mild steel welding operations are a significant source to the ambient air because of its uncontrolled nature, further research into reducing Cr(VI) during the welding process by utilizing changes to shield gas and electrode composition may be warranted.

INTRODUCTION

The present study was undertaken to update the existing base of emission factors for welding of steels, with particular emphasis on chromium in the +6 oxidation state, Cr(VI). Source tests were performed to improve the accuracy of the most critical emission factors. Commonly used welding materials and electrodes were employed with four types of welding operations: shielded metal arc welding (SMAW), gas-metal arc welding (GMAW), flux-cored arc welding (FCAW) and pulsed gas-metal arc welding (P-GMAW). Many parameters affect the quality of welds and their resulting emissions, far too many to be systematically varied for a range of welding processes and materials (Dennis et al., 1996, 1997; Quimby and Ulrich, 1999). As a consequence a decision was made early in the study to rely upon the expertise of skilled welders to determine conditions that would result in a good quality weld, and to test emissions under those conditions. The rationale for that decision being that welders strive to produce quality welds, not marginal welds from operating welding equipment at the extremes of what is possible.

Specific Objectives

Several initial objectives were outlined at the beginning of the study, including:

1) Establishing that welding procedures used in the study produce results comparable to those described in ANSI test method AWS F1.2:1999 (American Welding Society, 1999).

2) Comparing test results obtained with the standard ANSI/AWS procedure with those obtained from an enclosure designed and constructed at UC Davis that would allow extended run time and isokinetic sampling.

3) Establishing that the analytical procedure used to determine Cr(VI) in the study produces accurate and reliable results.

4) Conducting preliminary tests with high Cr-content welding electrodes and plates with AP-42 literature values run under similar conditions.

5) Conducting source tests on SMAW, GMAW, FCAW and P-GMAW with electrodes and under conditions used by California industries, focusing on stainless steel welding, a source of toxic hexavalent chromium,

BACKGROUND

Previous studies extensively examined the Fume Formation Rate, or Fume Generation Rate (FFR or FGR), historically expressed as an amount of fume produced per unit time of weld (Moreton et al. 1985; Malmqvist et al., 1986; IT Corporation, 1991). For emission inventory purposes, the California Air Resources Board (ARB) and United States Environmental Protection Agency (EPA) use a different approach: the mass of fume produced is related to the mass of wire consumed. Thus emissions are estimated from an emission factor and the quantity of welding electrode that a facility consumes (USEPA, 1994). As mentioned earlier, the types of welding processes commonly employed include SMAW, GMAW and FCAW. Technological advances have resulted in a shift away from utilizing SMAW and increased utilization of pulsed gas metal arc welding techniques (P-GMAW). For that reason, only a few SMAW tests were performed, mainly as a check on the historical values contained in the U.S. EPA's AP-42 database.

Welding Terminology

Shielded metal-arc welding (SMAW) uses an electrode that is shaped as a long thin rod and covered with a flux. For this reason, SMAW is also called “stick” welding. The electrode is attached to the welding machine clamps to establish the arc between the electrode and the welding surface. The outer covering of the electrode, when melted, creates the gaseous shield needed to protect the weld puddle from atmospheric contamination (Sacks, 1981).

Gas metal-arc welding (GMAW) is also referred to as MIG welding, and is probably the most widely used form of welding today (Quimby and Ulrich, 1999). GMAW allows for a continuous weld using a coiled spool of wire and a wire feeder to un-spool new wire as the electrode is consumed. Shielding gases such as carbon dioxide or mixtures of argon with carbon dioxide or oxygen are applied along the weld to protect it from atmospheric contamination.

Flux-cored arc welding (FCAW) is a combination of both SMAW and GMAW. It uses the wire feeding technique of GMAW, but the wire has an interior flux core which acts like the covering of an SMAW stick. As the electrode is consumed, it also creates the “shield” that protects the weld from oxygen, though shielding gas is normally also applied (Malmqvist, K.G. et al., 1986).

“Pulsed Welding” techniques utilize power supplies that switch between low voltage (amperage) and high voltage (amperage) during the welding process. This allows for a lower overall heat input and an improved molten pool and metal solidification. Thinner pieces of material can be joined with the added control. During long continuous conventional welds, the welding surface absorbs so much heat that the weld quality at the beginning of the weld differs from that at the end. That problem has largely been resolved using the pulsing technique (Street, J.A., 1990).

EXPERIMENTAL METHODS

Fume Collection

Two methods of fume collection were employed. First the American Welding Society (1999) test method F1.2:99 was applied. That method involves gas-metal arc welding of a standard electrode onto a rotating plate under a conical hood under specified voltage and electrode feed rates. Those conditions were used to establish that the welding conditions applied in this study could reproduce previously determined emissions under standardized conditions. Second, a welding enclosure through which air was drawn to capture total emissions isokinetically on a bank of high efficiency filters was utilized for the collection of samples for mass emission and chemical analyses. The enclosure and bank of filters extended the duration that a continuous welding operation could be conducted and included provision for isokinetic sampling from a section of ductwork that meets standard particulate matter sampling guidelines of at least eight stack or duct diameters downstream and two diameters upstream from any flow disturbance such as a bend.

For both systems, high efficiency glass fiber filters, commonly used for high volume air samplers (Whatman Glass Microfibre filters; EPM 2000) were used to collect the welding fumes. Filters were kept as clean as possible in their original container until use. When used, a filter was doubly wrapped in aluminum foil and pre-weighed. After testing, the filter was reweighed in its inner foil covering to determine the mass gained. Blanks were run to verify that Cr(VI) interference was not present on clean filters. Exposed filters were immediately extracted for soluble Cr(VI) after re-weighing. The filters were analyzed using a standard colorimetric method (Cal EPA, 1997) modified for flow injection analysis (FIA) (Wang et al., 1997; Lachat Instruments, 2000; ISO, 2002).

A constant flow rate onto the filters was maintained using standard “critical flow” hi-volume sampler Venturi orifices (GMW volumetric flow controller.). For each collection system, a Magnehelic® pressure gauge was attached to measure the pressure drop across the filters. Sampling was terminated if the pressure drop was greater than 40 inches water column (< 0.1 atm) in order to maintain a constant flow rate in the critical flow orifice by ensuring upstream pressure close to one atmosphere.

American Welding Society (AWS) Hood

A conical hood was constructed according to AWS specifications (American Welding Society, 1999). (See figure 1.) A slowly rotating turntable on which a metal plate was mounted provided a constant weld velocity that could be set prior to and maintained during testing. The welding gun was held in place on a stand such that the nozzle was located inside the “hood”, while the trigger was located outside for the welder to control the welding operation.

The AWS method calls for a filter medium that is a pad of glass fiber insulation 12 inches in diameter that acts as a “depth” filter. The efficiency of collection of that filter was checked by using it as a pre-filter ahead of a standard high efficiency glass fiber filter used for ambient hi-vol sampling. The mass captured by each filter could be compared and the pre-filter and total collection efficiencies determined. The pre-filter and glass filter are located about three feet above the welding surface. The mass recoveries were compared with that obtained by using a high efficiency hi-vol filter alone as well. Previous work has shown that while the glass fiber insulation pad collects the majority of the mass, some visible penetration through the pad occurs (Quimby and Ulrich, 1999). We observed similar findings, but depending upon the quality of the seal on the insulation pad, at times greater than 10% of the mass was collected on the hi-vol filter. For that reason, only hi-vol filter results, used to collect total mass and for extraction of Cr(VI), are reported in the emission factors.

A motor assembly is placed after the filter housing on the AWS hood. A Venturi orifice was used to regulate the flow rate to 40 cfm (slightly higher than the 35 cfm flow rate specified by the AWS method). Air is exhausted through the end of the hi-vol motor assembly. Additional tests to check for the possible presence of Cr(VI) in the gas phase utilized an air-tight “dryer” hose attachment that was secured with duct tape onto the end of the motor housing. A probe was inserted into the hose extension and gas samples were drawn through a gas impinger train described below to check for the presence of Cr(VI) in the vapor phase.

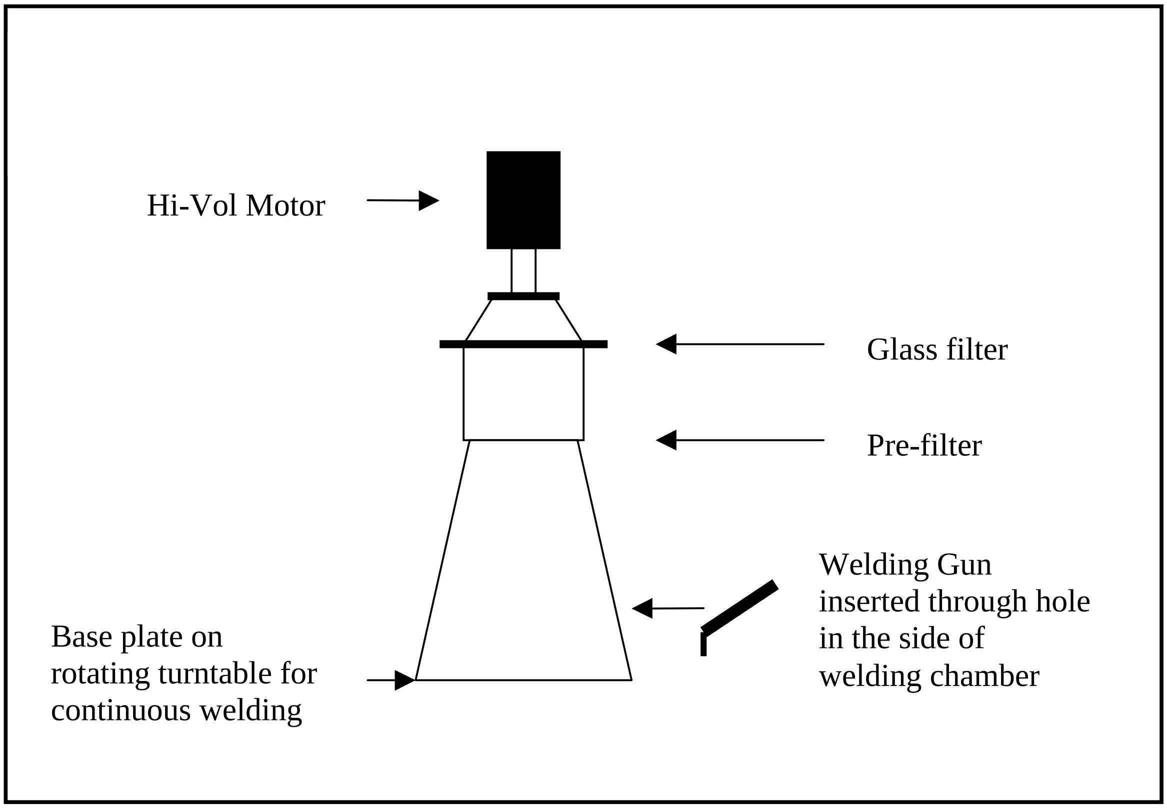

Figure 1. American Welding Society (AWS) Fume Hood.

UC Davis Enclosure

A rectangular welding enclosure 6 ft. by 4 ft. by 6.5 ft. was constructed of particle board on-site at the UC Davis campus. (See figure 2). The dimensions were selected such that a welder could stand and weld on a table that is on one end of the enclosure. For some tests, it was convenient to use a turntable with a circular metal plate and fixture for the welding gun, and to weld as was done for the AWS hood experiments. At other times it was easier for the welder to manually weld onto a separate plate. In either case, welding conditions were selected to provide a weld that would be "acceptable quality" in practice.

Air was ducted into a 2-foot diameter (60.5 cm) circular hole that was cut into the wall above the welding surface, and then through a conical transition into a 6 ft. (1.829 m) long, four in. (10.16 cm) ID pipe that led to a bank of four hi-vol filters. Another gradual transition section was added to match the flow to a rectangular plate that secured the filter bank. A flow-measuring device (Sierra Instruments, Inc. Model 441) was used to ensure that a reasonably uniform air flow rate was achieved across the entire inlet to the tunnel, but not so high as to disturb welding conditions on the bench surface (< 75 fpm or 0.5 m/s). (See Figure 3.) The velocity within the 4 in. (10.2 cm) duct was checked with a standard pitot tube against the total flow rate and conditions for isokinetic sampling were determined.

The filter bank consisted of four hi-volume filter housings and motors/pumps (only 2 are shown in Figure 2), each with a critical flow Venturi orifice to maintain a constant flow of 40 cfm (0.0189 m^3/s) for a total of 160 cfm (0.0755 m^3/s). Above and behind the welding table, rectangular openings were cut in the wall and ceiling to admit airflow into the enclosure. Each opening was covered with an air filter to minimize entrainment of potentially contaminated air into the enclosure. Blank runs with no welding taking place indicated no appreciable mass or Cr(VI) was in the background air. Since total flow was collected on the filter bank, the particle samples were inherently drawn onto the filters under isokinetic conditions.

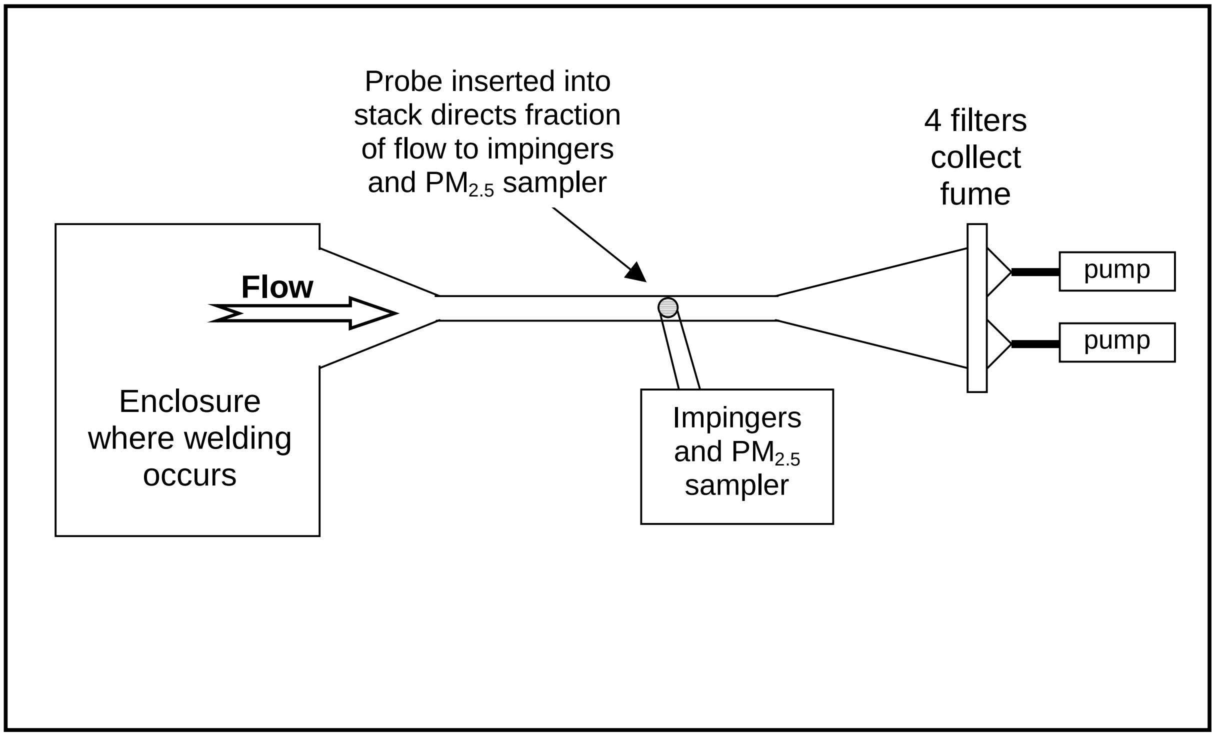

Figure 2. UC Davis enclosure illustrating test section for isokinetic sampling.

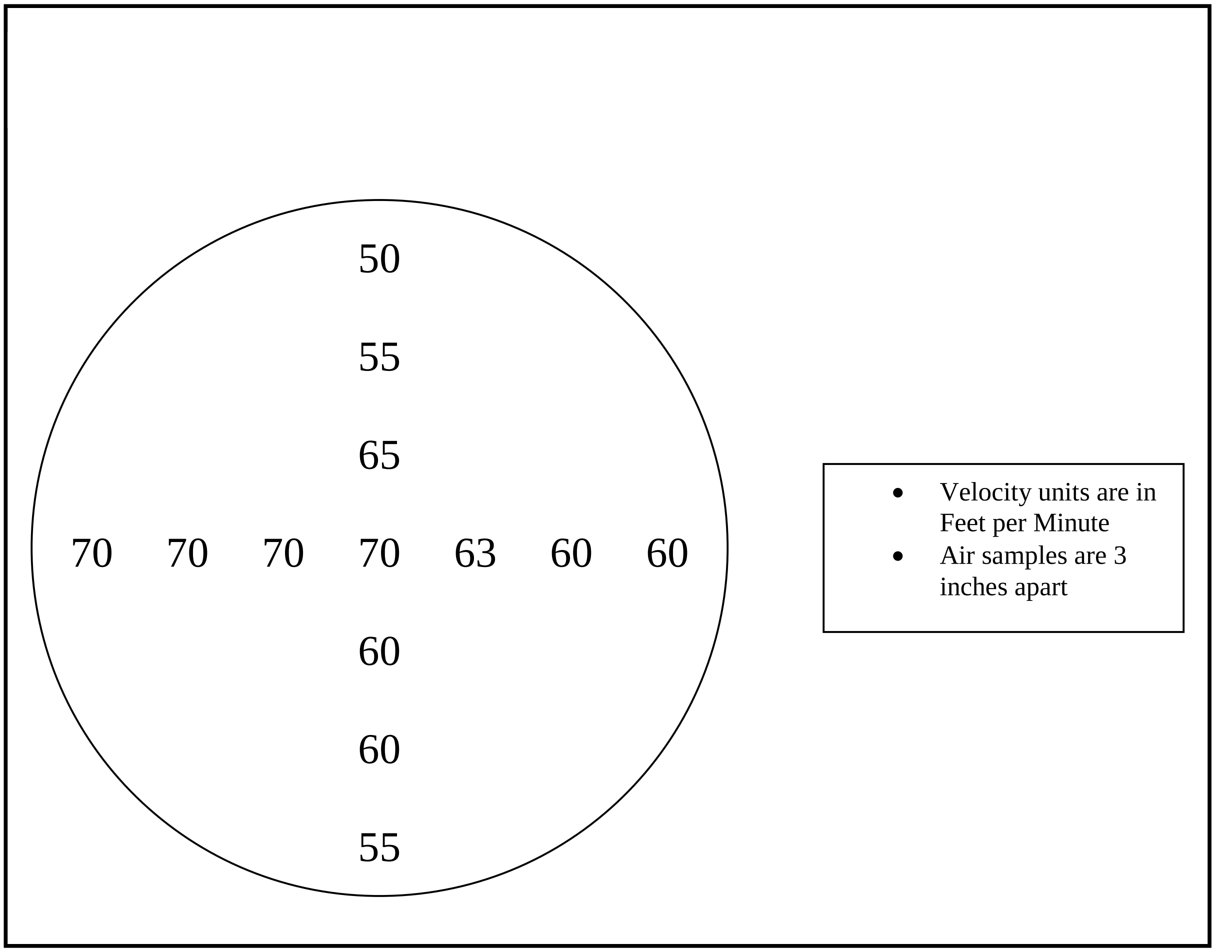

Figure 3. Flow rate into conical transition to isokinetic test section above welding bench in UCD enclosure.

PM 2.5 Testing

Air was drawn isokinetically from the sampling port in the 4-inch duct through a glass probe whose dimensions were selected to match the air velocity in the pipe extension from the enclosure. The air was sampled into an IMPROVE inlet system that separated particles larger than 2.5 microns at a flow rate of 23 LPM (0.023 m^3/min). Appendix A contains a description of the flow calibration procedure used by the UC Davis Crocker Nuclear Laboratory Air Quality group that supplied the sampler. The IMPROVE system was originally designed for ambient sampling and has four filter cassettes. Due to the high particulate matter concentration of the welding fumes it was necessary to utilize all four filters during the course of each test. Each filter was used for 15 seconds, a period short enough to maintain the desired particle cut-point of the cyclone inlet, but before the pressure drop on the teflon filters became too large to maintain the constant flow rate. Knowing the mass collected, a fume generation rate could be calculated for the IMPROVE system and compared to the fume generation rate of the UCD enclosure. The teflon filters were subsequently analyzed for total Cr and several other metals (Fe, Mn, Ni) by X-ray fluorescence.

Gas Phase Testing

A modified Method 425 sampling train (Cal EPA, 1997) was used to capture vapor phase chromium, if any formed. Four impingers were set up behind a sampling probe and filter housing, with a pump box of the impinger train. (See figure 4.)

Blanks were run before each test to ensure that Cr(VI) in ambient air would not be a factor in determining the chromium content. Because the Cr content of low Cr-containing welding electrodes and plates are inherently low, caution was exercised in handling the sampling equipment. (The chromium content of stainless electrodes is approximately 20%. By comparison, mild steel contains less than 1% chromium that occurs as an impurity if present at all, the standard steel electrode spool used in this study had a chromium content of 0.12% as determined by commercial lab analysis.) All glassware for the impinger train was washed, dried and covered with aluminum foil prior to use as a precaution against contamination.

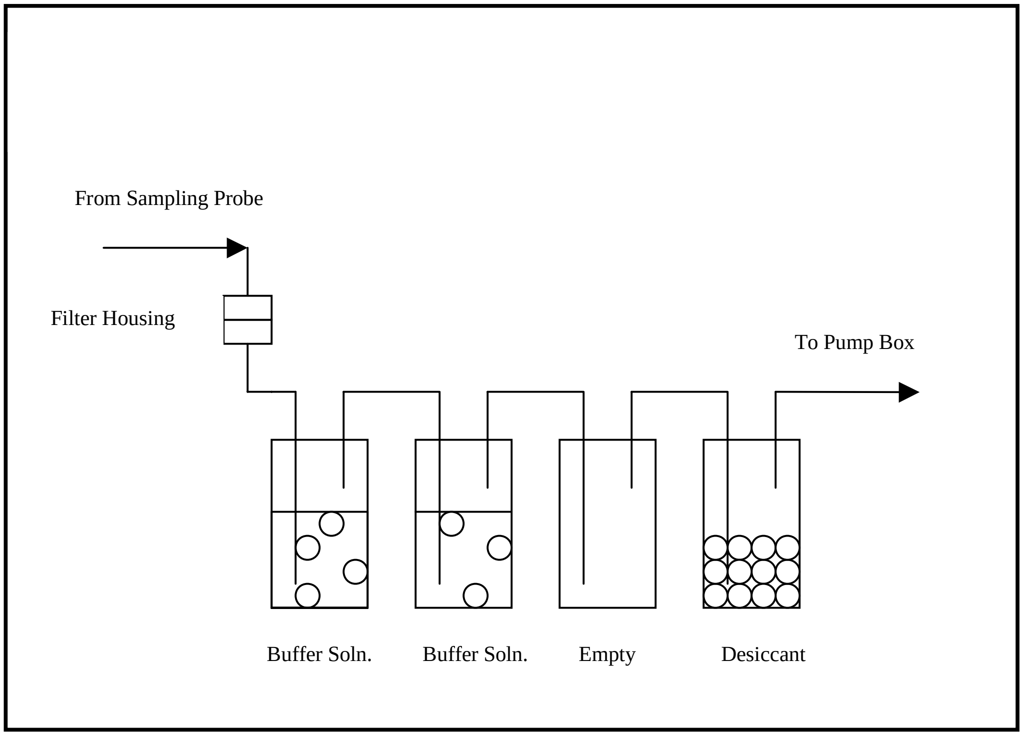

Figure 4. Impinger train used to check for possible presence of gas-phase Cr(VI).

Chemical Analysis

After a sampling run with the hi-vol filters, they were weighed and then immediately immersed in a neutral pH borate-buffer solution. A borate buffer was used in place of the usual bicarbonate buffer (Cal EPA, 1997; ISO, 2002; Wang et al., 1997) because of bubble formation in the detector of the flow injection analyzer (FIA). Bubbles resulted from mixing of the acidic colored reagent (diphenylcarbazide) immediately ahead of the detector, resulting in spurious signals. The stability of the borate buffer was determined by comparison with freshly prepared Cr(VI) standards and results were within 10% for periods up to one week and actually for several months. Samples were extracted and analyzed within 24-hours in most cases, but all samples were initially analyzed within three days.

The analytical procedures are described below.

(1) Preparation of buffer solution and color reagent: buffer consisted of 5.90 mL of 0.1 N NaOH and 50 mL of 0.1 M H_3BO_3 diluted to 100 mL; color reagent consisted of stirring 0.4g s-diphenylcarbazide with 200 mL isopropanol until it dissolved, followed by 720 mL water and 80.0 mL concentrated sulfuric acid in a 1.000 L volumetric flask and diluting to the mark with water.

(2) Preparation of standard solution: Stock solution was prepared with reagent grade potassium chromate (Fisher Certified) to a concentration of 100 mg Cr(VI)/L. Standard solutions were prepared for each analysis from the stock solution by dilution. The concentration of standards was 0.4, 0.2, 0.1, 0.05, 0.02, 0.01 and 0.0 mg-Cr(VI)/L..

(3) Sample extraction: The samples were extracted in an ultrasonic water bath for two hours. After extraction, the samples were passed through a 0.45 μm filter syringe filter as they were loaded into the sample tubes in order to minimize light attenuation by particle scattering in the detector. After further study, the large number of primary aerosol particles in the tens of nanometer size range required further filtration by 0.2 μm and 0.02 μm filters for low Cr-content rods. An estimate of the error introduced by particle scattering is provided with the data.

(4) Sample analysis: Samples were analyzed by QuickChem Flow Injection Analyzer Model 8000 (Lachat Instruments, 2000).

(5) The method detection limit was set at three times the area of a distilled water blank, which corresponded to 1 μg/L in the extracted solution, while the quantitation limit was set at 5 μg/L.

PM 2.5 XRF Analysis

The filters were analyzed using the Cu-XRF system at the UC Davis Crocker Nuclear Laboratory. The x-ray beam averages the signal over a 3.5 cm^2 deposit area of the filter and results are given as ng/cm^2 of deposit area. These filters were very heavily loaded, so that it was necessary to drop the x-ray current from the normal 10 mA calibration current to 1 mA. There is a slightly greater uncertainty regarding the accuracy of the measured concentration as a result. Results reported herein reflect the nominal uncertainty based upon a calibration at the normally higher current and thus should be considered qualitative for the elemental analysis. Gravimetric analysis of the fraction of PM 2.5 was not affected and ranged from about 20% to 60% of the mass being greater than 2.5 μm aerodynamic diameter.

RESULTS & DISCUSSION

Comparison between AWS Hood and UCD Enclosure with standard wire E70-S3

The AWS Hood method included a set of calibration tests, which specify all welding conditions including electrode, weld surface and current. Voltage was varied for three different series of tests. A fume generation rate (FGR) was determined for each test. Both the AWS Hood constructed for this project and UCD enclosure were tested under the specified conditions. The second column of Table 1 are the AWS literature reported values, the third column reports the FGR values determined by UCD using the AWS hood design, and the last column the FGR obtained using the UCD enclosure. The resulting FGR's were within 10% of the reported AWS values, thus both collection systems were deemed sufficiently accurate for further testing.

Table 1. Comparison of Fume Generation Rates (FGR) between UCD Enclosure and AWS Hood.

Voltage (V)	FGR AWS Hood (AWS)	FGR AWS Hood (UC Davis)	FGR UCD Enclosure (UC Davis)
24	0.43	0.452	0.417 ± 0.049
26	0.55	0.589	0.508 ± 0.019
28	0.63	0.684	0.627 ± 0.023

The AWS test method specifies use of a glass fiber insulation pad to collect welding fumes for subsequent gravimetric determination of fume generation rate (FGR). A back-up high volume filter was included in these tests (column 3) to determine whether there was significant penetration past the filter used in the AWS test procedure. A measurable amount of mass was collected on the hi-vol filters, on the order of 10%. However, the total mass collected by the pad and hi-vol filter was within 10% of the AWS result on the pad alone. As can be seen in column #3 above, our results are within 10% of the fume generation rates reported by the AWS for calibration, but are slightly higher. There are two possible explanations for the small differences. One is that the seal obtained with the insulation pad in our AWS-design hood may not have been as tight as that originally used by AWS, allowing a small fraction of particles to escape collection on the pad (Quimby and Ulrich, 1999). Second, the slightly higher inlet velocity, 40 cfm with the UCD AWS hood compared to 35 cfm for the AWS hood may have resulted in capture of a slightly greater amount of material that would otherwise have settled or deposited.

The results obtained with the UCD enclosure are well within 10% of the AWS hood results. There appeared to be a slight loss of aerosol, most likely by deposition to the walls of the "enclosure" during conveyance to the filters. However, we consider the losses to be negligible and likely comparable to what would occur in the workplace. While the duration of these tests was short, the results did not exhibit any noticeable dependency upon duration from continuous welding times about one-half to two minutes. That length of time is sufficiently long to be representative of a continuous weld for stainless steel. In the UCD enclosure, four "hi-vol" filters are used so that the duration of a test can be extended by a factor of four over use of a single "hi-vol" filter in the AWS hood. Thus we feel confident in our welding procedures, and that for purposes of an emission inventory, the errors in the data are negligibly small compared to other sources of uncertainty, e.g., uncertainties of actual welding conditions and uncertainties associated with the amounts of welding material consumed.

Cr(VI) Analysis

It was necessary to establish that the chemical analytical protocol for analyzing for Cr(VI) was accurate. An analysis procedure using the standard colorimetric reagent diphenylcarbazide (DPC) was developed for use with a flow-injection analysis (FIA) instrument (Lachat Instruments, 2000). Use of the FIA instrument improved reproducibility and reduced the potential for operator reading error.

The Air Resources Board has found that preservation of the soluble Cr(VI) is best accomplished in a near neutral buffer of sodium bicarbonate solution. In the FIA instrument, bubbles are formed when acidification with the DPC reagent occurs in the mixing cell. A different buffer system using sodium borate was substituted for the sodium bicarbonate in order to eliminate bubble formation in the detector. The results of tests of the borate buffer method are shown in figure 5 and table 2. The calibration curve and raw data from the FIA analysis, indicate that storage of the Cr(VI) sample in the borate buffer yields < 1% Cr(VI) loss for periods of at least 3 days. In general, filter or impinger Cr(VI) samples were analyzed within 24-hours. Often so much material was collected on each filter, that detection of Cr(VI) in the filter extracts was above within the upper calibration limit, and in some cases sample dilution was required in order to remain in the linear range of the standard curve. For additional quality control, standard filters loaded with known amounts of Cr(VI) were obtained from Danish IRRC and analyzed. The reported amount of Cr(VI) on those filters was 0.02945 mg per quarter filter. Our extractions and analyses of two quarter filters yielded 0.0259 and 0.0288 mg, within 10% of the standard filter (average error -7%). One additional series of tests was conducted to determine whether a borate buffer coating on a hi-vol filter would preserve any additional Cr(VI) compared to uncoated hi-vol filters. The results of those tests were within 2% for the emission rate, which was not a significant difference. Thus no coating of the hi-vol filters was deemed warranted.

Vapor Phase Chromium

The presence of vapor phase chromium was not anticipated since there was little or no chlorine present in the sample (Guo and Kennedy, 2001). Nevertheless the possible presence or lack thereof of vapor phase Cr(VI) was resolved by sampling using a modified Cal EPA Method 425 impinger train (CFR Title 40 Part 60 Appendix A-1). Vapors were drawn through the impinger train after the air stream was passed through the high efficiency glass fibers on the enclosure exhaust and through another glass fiber filter holder immediately ahead of the impingers. Prior to each test, a blank sample was run to check for any contamination that may have remained from previous testing. Samples for possible gas phase Cr(VI) were drawn for each type of welding process and results are shown in Table 2.

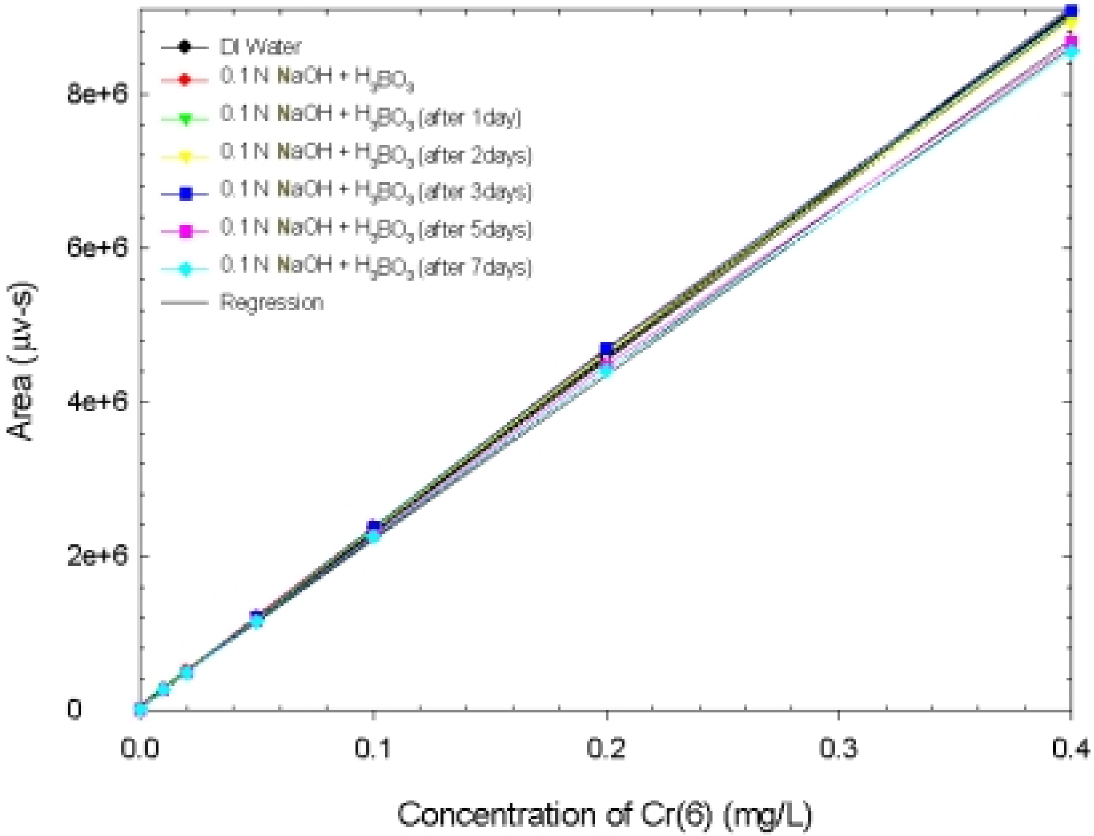

Figure 5. Calibration curve for Cr(VI) standard solution in distilled water and borate buffer.

The resulting vapor phase Cr(VI) measured less than one percent of the solid phase Cr(VI) in all samples. For those samples in which there appeared to be Cr(VI) above the detection limit, we believe the readings are actually due to small amounts of aerosol that penetrated through the two filter holders, or contamination of the impinger train during handling and not actually gas phase Cr(VI). Two "blank" runs had measured concentrations above detection limit and were of comparable magnitude to those reported in Table 2. In several tests, no Cr(VI) was recovered so the ratio of gas phase to particle phase Cr would be computed as zero. Those tests are listed in Table 2 as being less than the detection limit divided by the particulate Cr(VI) and are less than 3% of the aerosol Cr(VI) in all cases. The values in Table 2 demonstrate that for FCAW, SMAW and GMAW, whatever passes through the glass filters is negligible compared to the particulate phase Cr(VI) captured on the filters. Based on these results, we conclude that essentially all of the hexavalent chromium is associated with the aerosol and that for emission inventory purposes there are no significant gas-phase Cr(VI) emissions.

Table 2. Measurements of Vapor Phase Cr(VI).

Electrode	**Diameter**	**Cr(VI) Vapor / Cr(VI) Part**
Gas Metal Arc Welding (GMAW)		
E316L-Si	0.035 in	<0.027
E316L-Si	0.035 in	0.0077
E316L-Si	0.035 in	0.0073
Flux Cored Arc Welding (FCAW)		
E309LT-1	0.045 in	<0.023
E309LT-1	0.045 in	<0.024
Shielded Metal Arc Welding (SMAW)		
E316L-16	4 mm	<0.0013
E316L-16	4 mm	0.0072
E316L-16	4 mm	< 0.0025

High Cr-Content Wires and Rod Tests

For each type of chromium-containing electrode tested, an emission factor for Cr(VI) was calculated. The data are presented in Table 3. Emission factors are expressed in terms of mass of emission versus mass of electrode. It should be noted, that while emissions are related to the actual voltage and/or amperage and hence size of the electrodes and wire feed rates, for practical reasons an average emission factor was calculated using data collected from all the tests performed for various settings of the same type electrode and welding process. The SMAW tests (18% Cr content rod) resulted in a significantly greater portion of Cr(VI) per unit mass of welding rod consumed than any of the GMAW or FCAW tests (19% to 23% Cr-content wires). Because of the limited use of SMAW as reported by NASSCO (Sullivan, 2003), SMAW was not studied further. It should be noted that FCAW results reported in Table 3 represent values obtained with a shielding gas (100% CO_2). Industry representatives indicate use of shielding gas with FCAW is common practice (Sullivan, 2003). The effect of shielding gas will be discussed subsequently.

The results are also compared against an existing EPA database in Table 4 where data were available. The SMAW values are of interest because they permit comparison with earlier data contained in AP-42 (USEPA, 1994) as discussed below. Greater Cr(VI) emissions per unit mass of welding rod were also observed for SMAW (0.138 g-Cr(VI)/kg) than for FCAW (0.0142 g-Cr(VI)/kg) or GMAW (0.0068 g-Cr(VI)/kg) in tests performed for NASSCO (Sullivan, 2000).

Table 3. Emission Factors for Hexavalent Chromium.

Electrode	Diameter	Number of tests	Average Voltage (range)	Average Amperage (range)	Average Wire Feed Rate [in/min]	Grams Cr(VI)/ kg-Electrode (S.D. %)
Shielded Metal Arc Welding (SMAW)						
E316L-16	4 mm	4	not available	150 constant	not applicable	0.179 12.1%
Gas Metal Arc Welding (GMAW)						
E316L-Si	0.045 in	4	22.6 (21-24)	198 (165-225)	244 (210-280)	0.025 18.2%
E316L-Si	0.035 in	3	24.0 (23-24)	172 (134-214)	519 (311-774)	0.0086 45.2%
Fluxed Core Arc Welding (FCAW)						
E309LT-1	0.045 in	6	26.0 (25-26)	149 (146-155)	264 (262-266)	0.015 6.2%
Pulsed Arc Welding (P-GMAW)						
E316L-Si	0.035 in	5	23.7 (23-24)	128 (125-131)	370 (349-400)	0.012 25.3%
Mil 308L	0.045 in	3	26.8 (25-31)	174 (173-175)	245 (239-247)	0.027 70.5%

Table 4. Comparison with EPA Database Emission Factors (USEPA, 1994).

Electrode	**UC Davis**		**EPA**			
	Cr(VI) g/kg	Number of Tests	Total Cr g/kg	Cr(VI) g/kg	Number of Tests	Quality Rating
Shielded Metal Arc Welding (SMAW)						
E316L-16	0.179	4	0.522	0.332	2	D
Gas Metal Arc Welding (GMAW)						
E316L-Si	0.0194	7	0.528	0.010	2	D
Flux Cored Arc Welding (FCAW)						
E309LT-1	0.0146	6	n/a	n/a	n/a	n/a
E309LT-1 w/o shield gas	0.257	1				
E316-20	n/a	none	0.970	0.140	n/a	B

The FCAW (with gas shielding) and GMAW Cr(VI) emissions per unit mass of wire were comparable for both types of wires tested. The GMAW results obtained under similar, but not exactly identical conditions as in AP-42 (USEPA, 1994)[1] exhibited both a greater total fume generation rate and a higher concentration of Cr(VI) per gram of wire consumed, roughly double the amount per kg of wire. It should be noted however, that the AP-42 reported value is an average and exact electrode dimensions tested were not known. In this study for those values obtained under different conditions of voltage and amperage, especially for GMAW for which a larger number of tests were performed, the standard deviation of the emission factor was 45% for a given wire diameter when the voltage range was greater. The amount of Cr(VI) formed was also smaller for the smaller diameter wire by about a factor of two (0.035" *cf.* 0.045" dia.). Thus the Cr(VI) emission factors for GMAW are deemed to be in general agreement regarding the magnitude of the emission factor. The range of values reported in the separate studies are indicative of the inherent uncertainty in the average emission factors, about a factor of two higher and lower than the mid-range.

We suspect that the variation among the various runs is due to the lower current applied, hence lower temperature and reduced UV radiation emitted as oxygen mixes into the vapor and fumes (Dennis et al., 1997). Thus, besides the type and use of shield gas in current practice, the size of the required weld, hence the wire used, may alter the amount of Cr(VI) formed.

The single USEPA value reported for FCAW with a stainless steel rod is an order of magnitude higher than either the current study or the results submitted to the Air Resources Board by NASSCO. The latter two studies used the same shielding gas (100% CO_2) and the AP-42 value reported in the USEPA database are for self-shielded FCAW tests (USEPA, 1994), i.e., no shielding gas. One test of FCAW without shielding gas was performed at UCD and resulted in about a factor of 20 increase in the amount of Cr(VI) formed, approximately double the emission factor reported in AP-42. That result also appears in Figure 6.

Low Cr-Content Wire Tests

Electrode wire compositions are typically selected to match the metals being joined. In the case of mild steel, electrodes normally do not have Cr added. Its presence is only as an impurity in the manufacturing process, and not by design. For example, two common steel wire electrodes used in the tests are designated ER 70S-3 (GMAW) and E71T-1C (FCAW). Their standard nominal compositions are ER 70S-3: carbon 0.07%, silicon 0.7%, manganese 1.1%; and E71T-1C: carbon 0.05%, silicon 0.74%, manganese 1.0%, phosphorus 0.008%, sulfur 0.015%, with the balance being iron and traces of other impurities. For the spool of ER 70S-3 used in this study, the chromium concentration was determined to be 0.012% and the nickel concentration 0.011% by commercial laboratory analysis. As shown in Table 5, the initial analysis of these wire electrodes suggested that there were measurable amounts of Cr(VI) formed. However, upon subsequent additional filtration using a nominally rated 0.02 μm membrane filter, the concentration was reduced by over an order of magnitude, essentially nearer the detection limit of the method. In other samples with higher Cr concentration, filtration with a 0.02 μm filter only reduced the concentration by a few per cent. Thus we believe that the Cr(VI) concentration for the two steel wire electrodes is actually below the detection limit of the method, but some

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[1] Certain details of the original tests were not available in the reports, e.g., wire diameter, so it was impossible to reproduce the exact conditions.

small amount of residual light-scattering by particles was picked up by the detector and accounted for the signal observed.

Table 5. Raw Cr(VI) Extract Concentration After Filtration Through 0.45 μM and 0.02 μM Filter and Computed Emission Factors.

	0.45 um Filtered Solution		0.02 um Filtered Solution	
Electrode Description	Cr(VI) [mg/L]	Per Wire Mean - [ug/kg] Std Dev - [ug/kg]	Cr(VI) [mg/L]	Per Wire [ug/kg]
			Cr(VI) < indicated amount	
E70S-3	0.0252	1509	0.0035	185
0.045 in	0.0281	264	0.0031	17
	0.0364		0.0038	
	0.0263		0.0038	
E70S-3	0.0467	2174	0.0028	158
0.045 in	0.0400	228	0.0027	23
	0.0368		0.0036	
	0.0390		0.0027	
E70S-3	0.0827	4238	0.0019	150
0.045 in	0.0636	1030	0.0011	65
	0.0472		0.0034	
	0.0558		0.0024	
E71T-1C	0.0161	689	0.0096	416
0.045 in	0.0151	61	0.0097	14
	0.0154		0.0096	
	0.0183		0.0103	
E71T-1C	0.0155	1042	0.0091	401
0.045 in	0.0297	265	0.0091	16
	0.0255		0.0098	
	0.0272		0.0097	
E71T-1C		1592	0.0091	401
0.045 in	0.0371	9	0.0091	16
	0.0368		0.0098	
			0.0097	

The hypothesis that the residual signal was an artifact of light-scattering was further confirmed by the X-ray fluorescence analysis for total Cr in the PM 2.5 samples drawn for these wires. Table 6 summarizes filter analyses of the PM 2.5 for some GMAW and FCAW tests. No (Cr total chromium) was detected in those samples, much less Cr(VI). The estimated method detection limit for total Cr in the PM 2.5 filter samples corresponded to less than 100 μg-Cr/kg-electrode. The actual amount of Cr(VI) would be expected to be considerably lower.

An approach to estimating the Cr(VI) emissions from these low Cr-content wires would be to assume that the same fraction of Cr(VI) is formed and emitted with the fume as with the higher Cr-content rods. For example the average fraction of the total Cr emitted as Cr(VI) by GMAW was about 0.010%. Thus for an E71T-1C rod having a 0.012% Cr-content, an estimated fraction of 1.2 X 10^{-8} of the wire mass would be emitted as Cr(VI) or 12 µg-Cr(VI)/kg-electrode. That value is consistent with the non-detect values in tables 5 and 6.

Table 6. X-ray Fluorescence Analyses of Low Cr-Content Steel Electrodes.

XRF Analyses for Cr	**Cr** [ng/cm^2]	**Cr MDL** [ng/cm^2]	**Wire Wt** [g]	**Cr MDL/kg** [ug/kg]
GMAW	0.00	7.48	81.85	63.5
E70S-3	0.00	7.96	81.85	67.6
0.045 in	0.00	7.85	60.99	89.4
	0.00	7.77	60.99	88.5
FCAW	0.00	6.79	94.43	50.0
E71T-1C	0.00	6.80	94.43	50.0
0.045 in	0.00	5.47	92.83	41.0
	0.00	8.22	92.83	61.5

PM 2.5 Sampling Results

Samples were drawn to determine the fraction of the total mass collected that would be less than 2.5 µm in aerodynamic diameter (PM 2.5). While the primary particles that constitute the metal fume are much smaller, given their greater density and rapid coagulation of their high initial number concentrations yields significant amounts of particles greater than 2.5 µm. Table 7 presents the percentage of particles greater than PM 2.5 µm by welding process type and averaged over various conditions. Greater insight is obtained by examining the data as a function of the fume generation rate, since the shield gas flow rate was held constant at 35 cubic feet per hour (1.65 Lpm). Thus the initial mass concentration is directly proportional to the fume generation rate. It is evident in figure 6 that as initial mass concentration increases, the aerodynamic diameter of the particles increases. This must be the case because it can be shown from coagulation theory that the number concentration of primary particles of a few tens of nanometers diameter cannot be larger than about 10^8 particles per cubic centimeter for more than a few seconds. It appears that the P-GMAW gives rise to somewhat larger particles for a given fume generation rate. It may be that the pulsing of the input power also results in pulses of mass being vaporized so that although average power, hence temperature is lower, peak power and evaporative loss in the arc is just as great or greater. Hence even higher initial mass concentrations are present periodically in the gas. The initial coagulation rate is a function of the square of the initial concentration, which could account for the somewhat greater quantities of large particles for the same average FGR. It should be pointed out that while the PM 2.5 may be a significant fraction of the total mass, there are still large numbers of nano-sized particles present and the majority of the mass of particles still being less than PM 10.

Table 7. PM 2.5 Mass Measurements.

PM 2.5 Summary		
Process wire type	%-Greater than PM2.5 Average	Std Dev
GMAW E70S-3 0.045"	35.7%	8.3%
GMAW E316L-Si 0.045"	34.6%	7.6%
FCAW E71T-1C 0.045"	41.7%	12.1%
FCAW E309LT-1 0.045"	41.2%	3.2%
P-GMAW E316L-Si 0.035"	20.6%	1.3%
P-GMAW Mil 308-L 0.045"	57.4%	20.5%

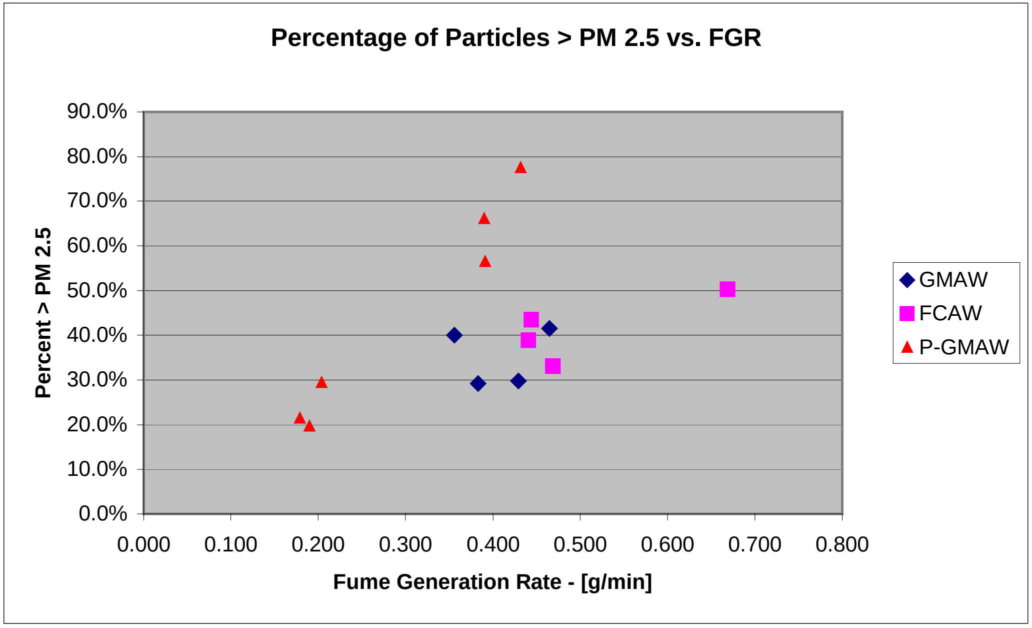

Figure 6. Percentage of particles larger than PM 2.5 as a function of fume generation rate.

Effect of Shield Gas Flow Rate

Numerous investigations of the effect of a shield gas have been performed (Dennis et al., 2002). In the present study two test series were performed with self-shielded welding electrodes (SMAW and FCAW). In both cases, the Cr(VI) emission rates per mass of electrode consumed were about an order of magnitude greater than in the presence of a shield gas. However, as explained earlier, SMAW or "stick" welding has largely been replaced by GMAW. Furthermore, while it is possible to perform FCAW with a self-shielding electrode, indications are that is not common practice (Sullivan, 2003). One series of tests illustrated in figure 7 was performed with FCAW to determine if increased shield gas flow rate would lead to reduced Cr (VI). Nominal shield gas flow rates of about 35 cfh are typical. As can be seen in the figure, by 20 cfh, the gain in Cr(VI) reduction has essentially been achieved. At the highest flow rate applied, 50 cfh, no significant reduction was observed and the total fume generation rate actually increased slightly as shown in figure 8. Thus simply increasing shield gas flow rate above that used in current practice will not reduce Cr(VI) emissions and may actually increase total particulate emissions.

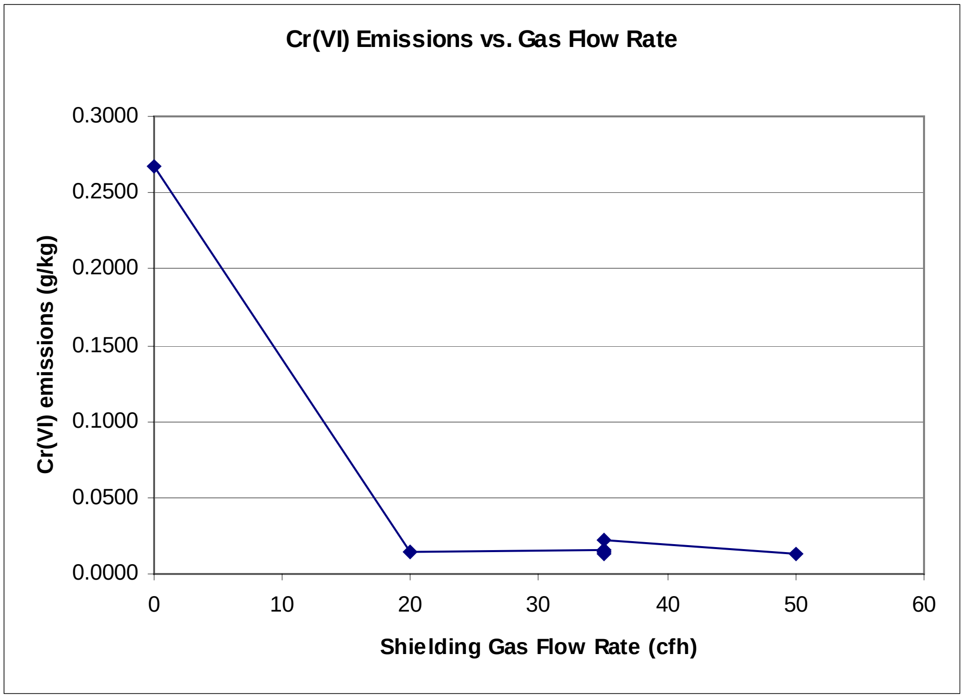

Figure 7. Effect of shield gas flow rate on FCAW Cr(VI) emission factor. Nominal shield gas flow rate is 35 cfh.

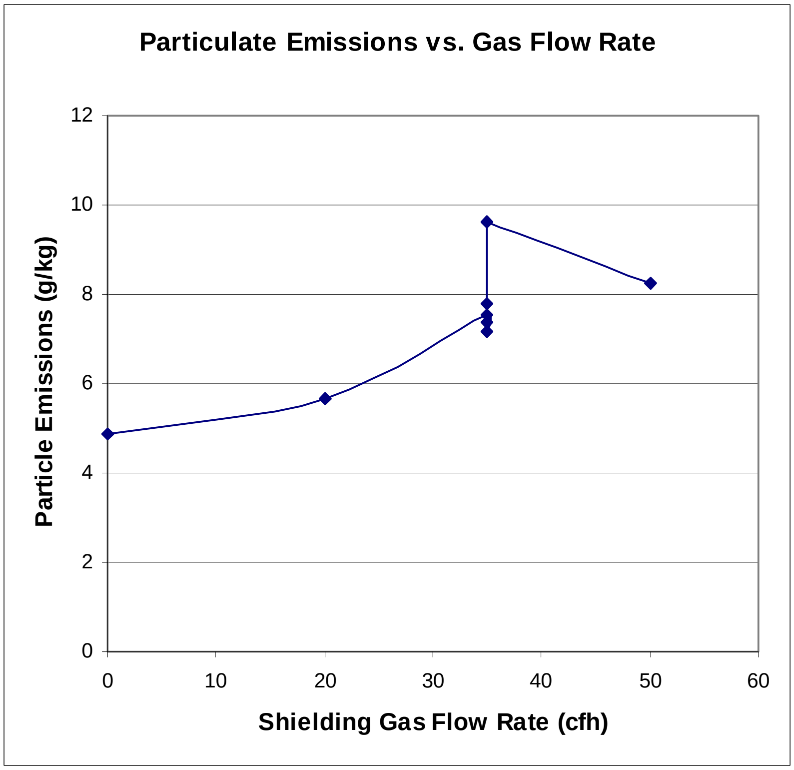

Figure 8. Effect of shield gas flow rate on FCAW total particle emission factor. Nominal shield gas flow rate is 35 cfh.

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APPENDIX A

IMPROVE PM 2.5 Sampler Calibration Procedure

The samplers flow rates are adjusted and calibrated at the time of installation and during annual maintenance. The calibration device is an orifice meter, which consists of an orifice and meter to measure the pressure drop across the orifice. The orifice is contained in a probe that is inserted at the base of the inlet stack. The calibration system is calibrated at Davis using a DryCal Nexus DC-2 Flow Calibrator that is certified NIST traceable. The log of the meter reading, M_o, is regressed against the log of the flow rate for a set of four flow rates covering the normal range of the device.

$$\log(Q) = a_o + \log\sqrt{\frac{T+273}{293}} + b_o * \log(M_o) \qquad \text{(Equation 1)}$$

At the time of installation, the nominal flow rates are adjusted to provide a flow rate of 23 L/min at 20°C with a typical filter in the cassette. Before any later re-adjustment, a 4-point calibration is performed. The equation for adjustment is:

$$M_o = \left(\frac{23}{F(elev)} \frac{1}{10^{a_o}} \right)^{1/b_o} \qquad \text{(Equation 2)}$$

Where: F(elev) corrects for atmospheric pressure at a given elevation; a_o and b_o are constants for the calibration meter. The technician adjusts the orifice diameter until the calibration meter has the desired reading.

The flow rate calibration compares the calibration device pressure drop and the pressure drop of each system transducer for four airflow settings covering the expected range. If the regression of the logs of these four points yields a correlation coefficient (R^2) less than 0.99, the system is recalibrated. The equation is:

$$\log(Q) = a_o + \log\sqrt{\frac{P(\text{sea level})}{P(site)} * \frac{T+273}{293}} + b_o * \log(M_o) \qquad \text{(Equation 3)}$$

PM 2.5 XRF Analyses

Results of the elemental analyses of the PM 2.5 filters by XRF for the metals Cr, Fe, Mn and Ni are presented in Table A-1. Note that these are qualitative estimates in that the filter samples were drawn for 15 seconds at a time while a total welding run duration might have lasted for a minute to a minute and a half. Thus there will be variability in the concentrations determined from filter to filter. The ratio of the elements should be relatively constant from one filter to the next within a given welding type. It is interesting to note that FCAW samples had a distinctively different Cr/Fe ratio than samples obtained by GMAW or P-GMAW. Also note that the column with the abbreviation MDL represents the method detection limit and was used as the basis for determining the absence of Cr in samples taken with standard mild steel welding electrodes.

Table A-1. Summary of XRF analyses of PM 2.5 welding aerosol samples.

Description	Estimated Cr Conc [mg/m^3]	Cr MDL [ug/m^3]	Fe total [mg]	Fe Conc [mg/m^3]	Cr/Fe	Wire [g]	Emission Factor Cr/Wire [g/kg]
Test 34, #2 GMAW Std	0.00	4.59	0.19	32.76	0.00	81.85	0.00
Test 34, #3 GMAW Std	0.00	4.89	0.21	36.98	0.00	81.85	0.00
Test 44, #1 FCAW Std	0.00	4.17	0.11	19.74	0.00	94.43	0.00
Test 44, #3 FCAW Std	0.00	4.17	0.10	17.65	0.00	94.43	0.00
Test 50, #1 FCAW Std	0.00	3.36	0.08	13.42	0.00	92.83	0.00
Test 50, #4 FCAW Std	0.00	5.05	0.16	27.59	0.00	92.83	0.00
Test 51, #3 FCAW	7.02	6.07	0.03	5.39	1.30	67.59	0.69
Test 52, #3 FCAW	8.28	6.58	0.04	6.46	1.28	67.41	0.81
Test 52, #4 FCAW	8.45	6.59	0.04	6.29	1.34	67.41	0.83
Test 53, #2 GMAW Std	0.00	4.82	0.19	32.78	0.00	60.99	0.00
Test 53, #3 GMAW Std	0.00	4.77	0.18	32.12	0.00	60.99	0.00
Test 54, #2 GMAW	10.35	8.57	0.12	21.53	0.48	76.48	0.96
Test 54, #3 GMAW	9.35	8.18	0.11	19.50	0.48	76.48	0.86
Test 55, #1 GMAW	7.41	7.07	0.09	15.73	0.47	64.17	0.68
Test 55, #2 GMAW	6.34	6.62	0.08	13.23	0.48	64.17	0.58
Test 59, #1 P-GMAW	3.20	4.79	0.04	6.31	0.51	58.93	0.33
Test 59, #3 P-GMAW	2.81	4.27	0.04	6.49	0.43	58.93	0.29
Test 60, #2 P-GMAW	5.69	6.14	0.07	12.02	0.47	58.57	0.59
Test 60, #3 P-GMAW	3.14	4.52	0.04	6.85	0.46	58.57	0.32
Test 61, #1 P-GMAW	4.76	5.70	0.06	11.10	0.43	56.81	0.43
Test 61, #3 P-GMAW	2.10	3.87	0.03	4.98	0.42	56.81	0.19
Test 62, #1 P-GMAW	4.88	5.72	0.07	12.08	0.40	56.58	0.44
Test 62, #3 P-GMAW	5.54	6.11	0.08	13.27	0.42	56.58	0.50

Table A-1 (Continued). Summary of XRF analyses of PM 2.5 welding aerosol samples.

Description	Estimated Mn Conc [mg/m^3]	Mn MDL [ug/m^3]	Mn/Cr	Wire [g]	Emission Factor Mn/Wire [g/kg]
Test 34, #2 GMAW Std	4.61	5.99		81.85	0.36
Test 34, #3 GMAW Std	5.18	6.50		81.85	0.40
Test 44, #1 FCAW Std	8.11	5.46		94.43	0.52
Test 44, #3 FCAW Std	8.49	5.36		94.43	0.54
Test 50, #1 FCAW Std	4.38	4.32		92.83	0.27
Test 50, #4 FCAW Std	10.89	6.69		92.83	0.67
Test 51, #3 FCAW	4.08	5.59	0.58	67.59	0.40
Test 52, #3 FCAW	4.64	6.04	0.56	67.41	0.46
Test 52, #4 FCAW	4.79	6.05	0.57	67.41	0.47
Test 53, #2 GMAW Std	4.63	6.24		60.99	0.38
Test 53, #3 GMAW Std	4.80	6.20		60.99	0.39
Test 54, #2 GMAW	7.37	8.67	0.71	76.48	0.68
Test 54, #3 GMAW	6.50	8.21	0.70	76.48	0.60
Test 55, #1 GMAW	5.25	7.17	0.71	64.17	0.48
Test 55, #2 GMAW	4.70	6.67	0.74	64.17	0.43
Test 59, #1 P-GMAW	3.36	4.83	1.05	58.93	0.35
Test 59, #3 P-GMAW	1.87	4.34	0.67	58.93	0.20
Test 60, #2 P-GMAW	3.79	6.23	0.67	58.57	0.39
Test 60, #3 P-GMAW	2.13	4.58	0.68	58.57	0.22
Test 61, #1 P-GMAW	3.27	5.80	0.69	56.81	0.29
Test 61, #3 P-GMAW	1.87	3.92	0.89	56.81	0.17
Test 62, #1 P-GMAW	2.93	5.82	0.60	56.58	0.26
Test 62, #3 P-GMAW	3.46	6.21	0.62	56.58	0.31

Table A-1 (Continued). Summary of XRF analyses of PM 2.5 welding aerosol samples.

Description	Ni Conc [mg/m^3]	Ni MDL [ug/m^3]	Ni/Cr	Wire [g]	Emission Factor Ni/Wire [g/kg]
Test 34, #2 GMAW Std	0.00	6.50		81.85	
Test 34, #3 GMAW Std	0.00	6.95		81.85	
Test 44, #1 FCAW Std	0.00	6.31		94.43	
Test 44, #3 FCAW Std	0.00	6.09		94.43	
Test 50, #1 FCAW Std	0.00	5.57		92.83	
Test 50, #4 FCAW Std	0.00	6.86		92.83	
Test 51, #3 FCAW	0.89	7.44	0.13	67.59	0.09
Test 52, #3 FCAW	1.03	7.79	0.12	67.41	0.10
Test 52, #4 FCAW	0.99	8.04	0.12	67.41	0.10
Test 53, #2 GMAW Std	0.00	6.63		60.99	
Test 53, #3 GMAW Std	0.00	6.75		60.99	
Test 54, #2 GMAW	4.01	11.93	0.39	76.48	0.37
Test 54, #3 GMAW	3.61	11.06	0.39	76.48	0.33
Test 55, #1 GMAW	2.83	10.06	0.38	64.17	0.26
Test 55, #2 GMAW	2.40	9.52	0.38	64.17	0.22
Test 59, #1 P-GMAW	0.76	7.31	0.24	58.93	0.08
Test 59, #3 P-GMAW	1.23	7.18	0.44	58.93	0.13
Test 60, #2 P-GMAW	1.95	9.44	0.34	58.57	0.20
Test 60, #3 P-GMAW	1.11	8.01	0.35	58.57	0.11
Test 61, #1 P-GMAW	1.33	8.59	0.28	56.81	0.12
Test 61, #3 P-GMAW	0.48	6.94	0.23	56.81	0.04
Test 62, #1 P-GMAW	1.19	9.15	0.24	56.58	0.11
Test 62, #3 P-GMAW	1.34	9.09	0.24	56.58	0.12

APPENDIX B

Nominal Welding Electrode Compositions

E70S-3
C = 0.07
Si = 0.7
Mn = 1.1

ER316L-Si
C = 0.022
Si = 0.85
Mn = 1.8
Mo = 2.45
Ni = 12.6
Cr = 19.25

Mil 308-L
C = 0.02
Mn =1.7
Si = 0.4
Cr = 20.5
Ni = 9.7

E71T-1C
C = 0.05
Si = 0.74
Mn = 1
P = 0.008
S = 0.015

E309LT-1
C = 0.03
Si = 0.45
Mn = 1.05
Mo = 0.1
Ni = 13.5
Cr = 23
Cu = 0.1
P = 0.02
S = 0.016

E316L-16
C = 0.02
Si = 0.48
Mn = 1.05
Mo = 2.3
Ni = 13
Cr = 18
Cu = 0.2
P = 0.015
S = 0.015

Appendix C

Experimental Advanced Light Source X-Ray Analysis of Welding Aerosol

Development of a non-destructive physical analytical method to distinguish chromium oxidation state is under development by Dr. Stephan Friedrich of the Lawrence Livermore National Laboratory (LLNL) using the Advanced Light Source (ALS) at the Lawrence Berkeley Laboratory (LBL). The method that monitors Cr L-edge x-ray emissions, by scanning the energy of the incident X-ray beam from 560 to 600 eV and recording an X-ray fluorescence (XRF) spectrum for each incident energy with a new superconducting tunnel junction (STJ) spectrometer, and plotting the (normalized) intensity of the fluorescence. (This is often labeled Partial Fluorescence Yield, or PFY.) Besides neat Cr samples of varying oxidation states, three welding aerosol samples were supplied by the current project: Danish welding Cr(VI) reference aerosol; one filter from test #44 – mild steel FCAW sample; one filter from test #51 – FCAW stainless steel sample. Dr. Friedrich analyzed these samples at no cost to the project. The results are reported below for completeness.

Test #44 did not have a detectable amount of Cr in the sample (data not shown), consistent with the Crocker Nuclear Laboratory XRF data and the expected low level of Cr in the mild steel welding electrode, E71T-1c. Figure C-1 illustrates the results obtained from test #51, FCAW using an E309LT-1 electrode in comparison with two Cr solid standards containing Cr(III) and Cr(VI). The standards were measured by total Auger electron yield (TEY), which has a different intensity ratio between the left half (edge L3) and right half (edge L2) of the spectrum than fluorescence. Differences in self-absorption can also affect relative intensities, when an element is present with locally high concentrations versus when the element is dispersed uniformly throughout a sample.

The Cr present in sample #51 appears to be primarily Cr(III). There is essentially no resolvable Cr(VI) signal in spectrum obtained from sample #51, though there is a slight hint of a small change from the Cr(III) sample. Sample #51 is compared with the Danish reference aerosol and the Cr(III) standard in Figure C-2.

As can be seen, there is a distinct peak due to Cr(VI) in the Danish Cr(VI) standard. An estimate of the amount Cr(VI) in sample #51 indicates it represents only about 0.15% of the total mass of aerosol and perhaps 2% of the Cr. Thus while the use of the ALS for determination of Cr oxidation state is promising, the detection limit in the presence of large amounts of other Cr forms is insufficient for quantification at the percent level. The method is still under development and at a future time may have improved sensitivity.

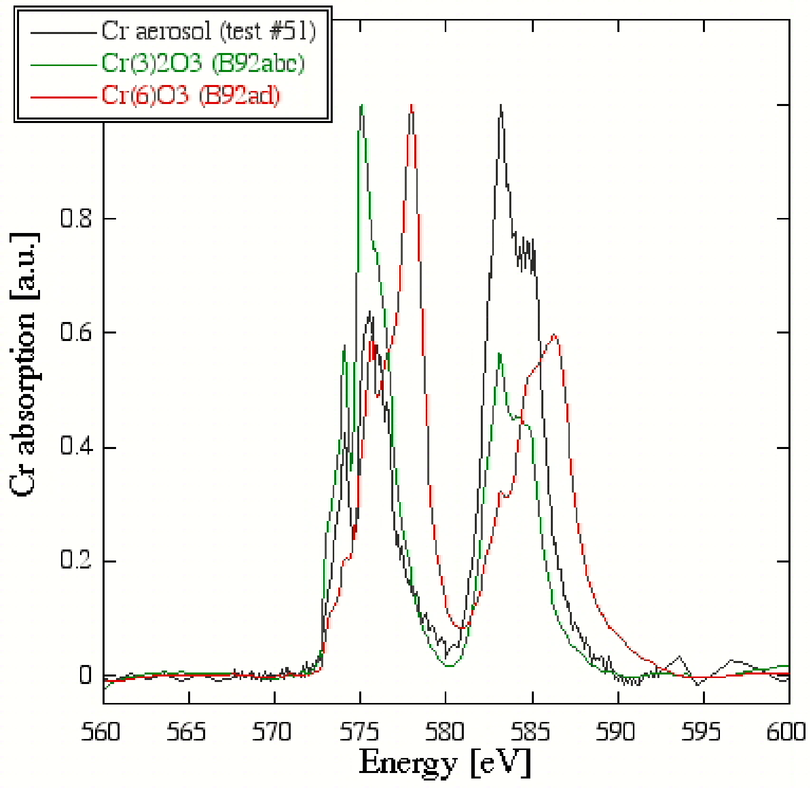

Figure C-1. Comparison of test #51 stainless steel FCAW welding aerosol sample with two samples containing Cr(III) and Cr(VI) respectively.

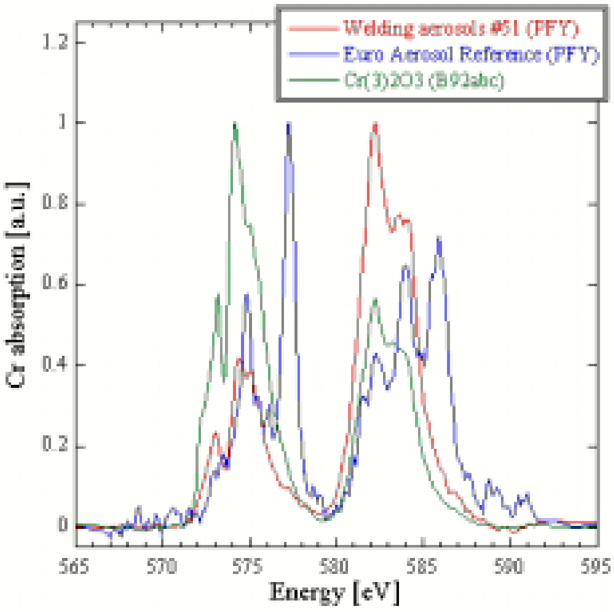

Figure C-2. Comparison of test #51 stainless steel FCAW welding aerosol sample with Danish welding aerosol reference and neat standard containing Cr(III).