

# Characterizing Exposures to Airborne Metals and Nanoparticle Emissions in a Refinery

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An air quality survey was conducted at a precious metals refinery in order to evaluate worker exposures to airborne metals and to provide detailed characterization of the aerosols. Two areas within the refinery were characterized: a furnace room and an electro-refining area. In line with standard survey practices, both personal and area air filter samples were collected on 37-mm filters and analyzed for metals by inductively coupled plasma–atomic emission spectroscopy. In addition to the standard sampling, measurements were conducted using other tools, designed to provide enhanced characterization of the workplace aerosols. The number concentration and number-weighted particle size distribution of airborne particles were measured with a fast mobility particle sizer (FMPS). Custom-designed software was used to correlate particle concentration data with spatial location data to generate contour maps of particle number concentrations in the work areas. Short-term samples were collected in areas of localized high concentrations and analyzed using transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) to determine particle morphology and elemental chemistry. Analysis of filter samples indicated that all of the workers were exposed to levels of silver above the Occupational Safety and Health Administration permissible exposure limit of  $0.01 \text{ mg m}^{-3}$  even though the localized ventilation was functioning. Measurements with the FMPS indicated that particle number concentrations near the furnace increased up to 1000-fold above the baseline during the pouring of molten metal. Spatial mapping revealed localized elevated particle concentrations near the furnaces and plumes of particles rising into the stairwells and traveling to the upper work areas. Results of TEM/EDS analyses confirmed the high number of nanoparticles measured by the FMPS and indicated the aerosols were rich in metals including silver, lead, antimony, selenium, and zinc. Results of the survey were used to deduce appropriate strategies for mitigation of worker exposure to airborne metals.

*Keywords:* aerosol; aerosol mapping; metals; particle; ultrafine

## INTRODUCTION

Some of the intrinsic properties of metallic elements, such as electrical conductivity, hardness, or catalysis, have made metals an integral part of modern industrialized society. Other properties render the metals toxic, with potential to impact the health of workers that mine them (Brune *et al.*, 1980; Thomassen

*et al.*, 1999) or prepare them for use by the rest of society (Linnainmaa *et al.*, 1996; Chadwick *et al.*, 1997; Zimmer and Biswas, 2000; Drake and Hazelwood, 2005; Harris *et al.*, 2005). In an effort to minimize the health impacts of metals on workers, particularly airborne metals, occupational exposure limits have been developed to minimize or mitigate the hazards posed by workplace exposures (OSHA, 1989; NIOSH, 2005; ACGIH, 2008). In order to appropriately measure workers' exposure to airborne metals, standard methods of analysis have also been developed. The

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International Organization for Standardization (ISO) method 15202 (ISO, 2000; ISO, 2001; ISO, 2004) was designed for analyzing air filter samples for metals and metalloids, including soluble compounds, whereas the National Institute for Occupational Safety and Health (NIOSH) method 7303 (NIOSH, 2003) was designed for measuring total metals on filter samples.

Analytical methods usually include protocols for the collection of representative samples to determine worker exposures. Typically, the standard methods describe collection of filter samples for specified periods of time in the breathing zone of individual workers while they are performing their normal duties. Area filter samples in selected work areas are often collected as well, and both types of samples are analyzed for the contaminant of interest. Researchers continue to investigate the validity and quality of the samples collected that evaluate a worker's breathing zone (Clinkenbeard *et al.*, 2002; Ashley *et al.*, 2003). Occasionally, additional data are gathered using alternative techniques such as the collection of real-time samples to deduce task-specific exposures (Martinelli *et al.*, 1983), continuous automated sampling to provide round-the-clock data acquisition (Samanta *et al.*, 2001), or the generation of spatial maps from the data (Evans *et al.*, 2008).

There is considerable toxicity information available regarding airborne metals; however, the effect of the particle size on biological responses is only recently becoming better understood (Cheng, 2004; Sivulka *et al.*, 2007; Nurkiewicz *et al.*, 2008). The need to measure the size distribution of the particles during workplace surveys is becoming increasingly important as awareness increases and more information regarding the hazards of ultrafine particles becomes available, since they have the potential for enhanced bioavailability and thus detrimental health effects (Oberdoerster, 2001; Ibaldo-Mulli *et al.*, 2002). In response to this concern, NIOSH has begun to focus some of its research on the development of new techniques for workplace surveys, particularly regarding characterization of nanoaerosols.

In the current work, the authors set out to demonstrate the use of additional tools to enhance the results of a standard workplace survey, with a focus on developing a robust yet streamlined and portable system for evaluating airborne hazards in the workplace. The approach employs three distinct tools. The first of these tools entails making workplace measurements of particle number concentration using a TSI Model 3091 Fast Mobility Particle Sizer (FMPS), along with the use of custom-designed software for logging the data and generating two-

dimensional tomographic maps of the information. The second tool involves using a data-logging photometer to gather time-resolved information about airborne particle mass concentration. The third tool entails 'informed sampling', i.e. the collection of particulate samples at key locations in the workplace using a handheld electrostatic precipitator (ESP) and subsequent detailed characterization of the aerosols via analysis of collected samples using transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). By applying these tools along with the standard filter sampling approach, we were able to generate additional valuable information regarding the number, size, morphology, and fate of ultrafine workplace aerosols.

To evaluate this new approach, a workplace survey was conducted in which these tools were used side-by-side with the standard (filter sampling) method in order to evaluate the potential benefits of the approach. The survey entailed evaluating worker exposure to airborne metals resulting from operation of furnaces and an electro-refining process during purification of silver at a precious metals refinery.

## METHODS

### *Process description*

The precious metal processing facility uses a three-stage process to refine silver. A high-volume furnace is used to melt the incoming feedstock, which is metallic silver with some impurities. This furnace is located on the first floor of the building and employs a local ventilation system to control worker exposures by capturing furnace fumes using an airflow drawn through a cowl installed around the furnace. Up to 1200 kg of silver feedstock per batch are melted slowly over a period of a few hours. Subsequently, over a period of ~50 min, the molten metal is poured into molds which have been preheated with a propane torch. The molds are specially shaped to form plates of silver, which become the anodes in the electro-refining process used to purify the silver. After cooling, these anode plates are transferred to the second level of the building, where they are placed opposite from stainless steel cathodes in an ion exchange cell, consisting of a nitric acid bath. A voltage potential is applied across the electrodes that oxidizes the impure silver anodes and grows silver crystals on the stainless steel cathodes in each of the individual ion exchange cells. After deposition is complete, the silver crystals are removed from the cathodes and transported back to the high-volume furnace to be made into anodes for further refining or to a low-volume furnace, also located on the main floor, to be melted and molded

into ingots, which is the final product from this facility. The low-volume furnace is located in a large local ventilation plenum, which draws the fumes away from the workers.

#### Filter sampling

Filter samples were collected to determine the workplace levels of metals, including both total silver and soluble silver compounds. In the USA, the Occupational Safety and Health Administration (OSHA) established a permissible exposure limit (PEL) of  $0.01 \text{ mg m}^{-3}$  for all forms of airborne silver. The NIOSH also set their recommended exposure limit (REL) for silver at  $0.01 \text{ mg m}^{-3}$  (OSHA, 1989; NIOSH, 2005). However, the American Conference of Governmental Industrial Hygienists (ACGIH) established a threshold limit value (TLV) of  $0.1 \text{ mg m}^{-3}$  for metallic silver and  $0.01 \text{ mg m}^{-3}$  for soluble silver

compounds (ACGIH, 2008) (Table 1). Although no OSHA PEL exists for soluble silver compounds, it is more toxic than metallic silver (Drake and Hazelwood, 2005) and the ACGIH TLV for metallic silver, while not a formal standard, is 10 times higher than the PEL for total silver. In order to differentiate between the two forms of silver, two analytical methods were used in this study. The NIOSH method 7303 (NIOSH, 2003) was used for deriving total metals, including silver, and the ISO method 15202 (ISO, 2000; ISO, 2001; ISO, 2004) was used to analyze some of the area filter samples for soluble silver compounds.

Personal samples were collected over a full work shift on six employees, two working on the electro-refining floor and four working on the furnace floor (Table 1). Each sample was collected on a 37-mm mixed cellulose ester filter, housed in a closed-face

Table 1. Occupational exposure limits for the metals detected by NIOSH method 7303, along with airborne metal concentrations ( $\text{mg/m}^3$ ) derived from personal filter samples. Concentrations in bold are above the OSHA PEL. Letters A–N indicate the location of the area samples in Figs 1–5.

	Antimony	Copper	Iron	Lead	Silver	Soluble silver	Zinc
OSHA PEL	0.5	0.1	10	0.05	0.01		5
NIOSH REL	0.5	0.1	5	0.05	0.01		5
ACGIH TLV	0.5	0.2	5	0.05	0.1	0.01	2
Personal sample results							
Electro-refining floor	<sup>a</sup>	0.071	0.023	0.003	<b>0.049</b>		0.010
Electro-refining floor	<sup>a</sup>	0.095	0.045	0.004	<b>0.094</b>		0.001
High-volume furnace operator	0.003	0.013	0.017	0.006	<b>0.029</b>		0.001
Furnace floor, forklift operator	0.003	0.006	0.006	0.004	<b>0.013</b>		0.001
Chemistry lab; furnace floor	<sup>a</sup>	0.008	0.009	0.002	<b>0.038</b>		0.001
Low- and high-volume furnace operator	0.002	0.007	0.007	0.005	<b>0.018</b>		0.001
Area sample results							
Furnace floor							
A—near high-volume furnace	0.003	0.006	0.002	0.005	<b>0.017</b>		0.001
B—between furnaces	0.002	0.006	0.005	0.005	<b>0.013</b>		0.001
C—across from high-volume furnace	0.003	0.008	0.003	0.009	<b>0.015</b>		0.001
D—across from low-volume furnace	0.003	0.007	0.003	0.007	<b>0.017</b>		0.001
E—15 m from furnaces	0.003	0.006	0.002	0.005	<b>0.013</b>		0.001
F—near low-volume furnace	0.003	0.007	0.003	0.005	<b>0.017</b>		0.001
G—near stairwell	0.005	0.012	0.002	0.015	<b>0.022</b>		0.001
H—near low-volume furnace	<sup>a</sup>	0.006	0.005	0.004	<b>0.039</b>		0.002
Electro-refining floor							
I—above ion exchange cells	<sup>a</sup>	0.008	0.003	<sup>a</sup>	0.006	0.002	0.001
J—above ion exchange cells	<sup>a</sup>	0.011	0.002	<sup>a</sup>	0.006	0.001	0.002
K—above ion exchange cells	<sup>a</sup>	0.012	0.003	<sup>a</sup>	0.007	0.002	0.002
L—above ion exchange cells	<sup>a</sup>	0.009	0.002	<sup>a</sup>	0.006	0.001	0.001
M—15 m from ion exchange cells	<sup>a</sup>	0.005	0.002	<sup>a</sup>	0.004		0.001
N—cell maintenance, cleaning	<sup>a</sup>	0.031	0.006	0.004	<b>0.012</b>		0.005

<sup>a</sup>Below the limit of quantification.

plastic sampling cassette. Using plastic tubing, the cassette was connected to a medium flow-rate pump, which was attached to the worker's belt and calibrated at  $2.0 \text{ l min}^{-1}$ . The cassettes were clipped to the workers' collars so that air from their breathing zone could be collected. All personal samples were analyzed using the NIOSH method 7303 (NIOSH, 2003). This method entails a strong acid digestion of the filter samples and analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Concurrently with personal sampling, 8 area samples were also obtained on the furnace floor and 10 on the electro-refining floor to evaluate exposure zones and the range of airborne metal concentrations throughout the refinery (Table 1 and Fig. 1–5). The area samples on the furnace floor and six of the samples from the electro-refining floor were analyzed using NIOSH method 7303 (NIOSH, 2003). The remaining four samples from the electro-refining floor were collected on 37-mm polytetrafluoroethylene filters housed in an opaque closed-face plastic sampling cassette and analyzed using ISO Method 15202 for soluble silver (ISO, 2000; ISO, 2001; ISO, 2004). In this method, deionized water is used to extract the soluble metal compounds followed by ICP-AES analysis. The levels of soluble silver were of particular interest in this study due to the possibility of aerosolization of the liquid in the electro-refining process.

### *Aerosol characterization*

Airborne particle concentrations (particles per cubic centimeter air) on the furnace floor and the electro-refining floor were measured throughout the day using a FMPS mounted on a cart that was moved to a new location approximately every minute. The FMPS took a continuous sample at a vertical height equivalent to a worker's breathing zone and measured the size distribution of particles between 5.6 and 560 nm at a frequency of 1 Hz.

Data were collected by the FMPS for  $\sim 1$  min at each location and synchronized with location data recorded into a laptop-based mapping system. The mapping system comprised custom software designed to allow the user to import a plan view map of the workplace, click a location on the map, and link data to that location. The combined data were used to generate contour maps of particle number concentration, based on a distance-weighted interpolation scheme between data points (Fig. 1–5). Each map represents data gathered at 12–20 selected locations, spaced  $\sim 3$  m apart throughout each floor of the refinery. The number and spacing of sampling locations were chosen to allow measurement at all locations on each floor over

a total time period of 15–30 min, so the maps represent 'snapshots' of particle concentration in the workplace during that time period. This mapping technique was used to investigate the fate of airborne particles within the plant and to help identify areas of higher concentrations for more focused short-term sampling and particle characterization.

Short-term particle samples were collected over 5–50 s periods at selected locations, identified during the mapping process, using a handheld ESP being developed by the authors. Each sample from the ESP consisted of particulate deposition onto a 400 mesh copper TEM grid coated with SiO film, which was analyzed for particle size and morphology (shape) using a TEM. The samples were also analyzed using EDS to provide the elemental content for a number of selected particles. The analyses were done using a Philips CM12 microscope equipped with a Power MX EDS system (EDAX, Inc., Mahwah, NJ, USA).

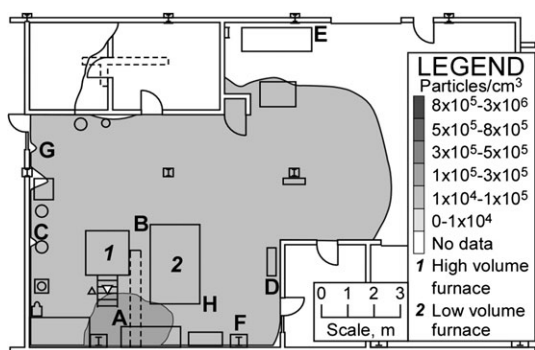
Real-time data regarding the mass concentration of airborne particles were also collected throughout the day, using two light-scattering photometers. The photometer chosen for this survey was the Thermo Electron Personal DataRAM 1200 (PDR). The PDR is a small lightweight instrument designed to be attached to a workers belt and operated as a passive sampler. It can also be used as an active sampler for taking area samples as was done for this survey. For active sampling, an auxiliary pump was used to draw air over the sensor, and a cyclone (BGI Model GK 2.05) was attached to remove larger particles, i.e. those  $>5.5 \mu\text{m}$ . The PDR gives the best sensitivity in the respirable range, is auto ranging between  $0.001\text{--}400 \text{ mg m}^{-3}$ , can sample as fast as 1 Hz, and has built-in data-logging capability.

Two PDRs were used to collect area-based data, one located on the upper level between two of the ion exchange cells (next to area filter sample J in Figs 4 and 5) and one on the lower level near the high-volume furnace (next to area filter sample A in Figs 1–3). The PDRs are factory calibrated using SAE Fine (ISO Fine) dust, and thus, the measured data do not accurately reflect the mass concentration of the metallic particles. However, data from the two PDR photometers do provide a valuable indicator of trends in approximate mass concentration.

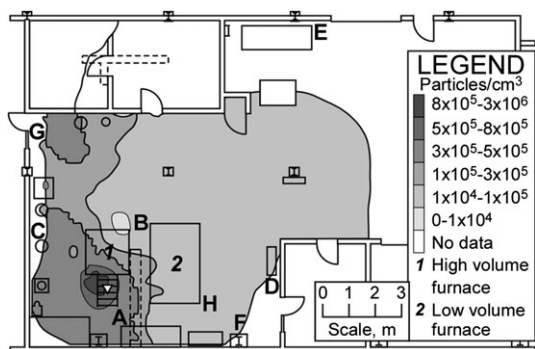
## RESULTS

### *Filter samples*

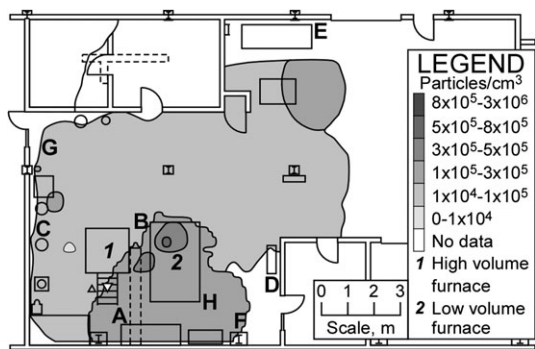
Of the many elements analyzed on the personal filter samples using the NIOSH Method 7303



**Fig. 1.** Map of particle number concentration generated at start of shift (8:00 AM), which constitutes baseline data for the furnace floor. Letters A–H are the locations for the area filter samples.



**Fig. 2.** Map of particle number concentration generated during the first pour of molten silver into an anode mold. Letters A–H are the locations for the area filter samples.



**Fig. 3.** Map of particle number concentration during pouring of refined silver ingots. Letters A–H are the locations for the area filter samples.

(NIOSH, 2003), only a small number had concentrations above the quantification limit for the method (Table 1). The only metal with concentrations in excess of the NIOSH REL and the OSHA PEL

was silver. Similarly, analysis of the area samples showed that the range in mass concentration of total silver was 0.013–0.039 mg m<sup>-3</sup> on the furnace floor and 0.004–0.012 mg m<sup>-3</sup> on the electro-refining floor, while levels of all other metals were significantly less than the PELs (Table 1). All area samples analyzed for soluble silver compounds were <0.002 mg m<sup>-3</sup>.

### Aerosol mapping

Airborne particle number concentration data were collected beginning at 8:00 AM while the high-volume furnace was warming up. The mapped data (Fig. 1) show that particle concentrations were slightly higher around the furnace, but overall, the concentrations were relatively low. That initial survey provided a baseline level of particle number concentration for the furnace floor, in the range of  $\sim 5 \times 10^3$  –  $5 \times 10^4$  particles cm<sup>-3</sup>.

The particle number concentration on the main floor rose as the high-volume furnace heated up and the feedstock began melting. During the pouring of the molten feedstock into the anode molds, the particle concentrations reached the highest level and the peak of the particle size distribution decreased from a mean diameter of  $\sim 100$  nm for baseline measurements to  $\sim 10$  nm near the furnace. The map generated at the beginning of the first pour (Fig. 2) shows concentrations  $>10^6$  particles cm<sup>-3</sup> around the furnace and anode mold areas.

Particle number concentration data were also collected during the pouring of refined silver ingots. The map generated  $\sim 2:00$  PM during the pouring of ingots is shown in Fig. 3 and indicates that the areas of high particle concentration were again limited, in this case to the region immediately adjacent to the low-volume furnace and ingot mold trays.

A map of the particle number concentration on the electro-refining floor, generated from data collected at  $\sim 9:00$  AM (Fig. 4), shows particulate levels similar to the baseline levels on the furnace floor. Data collected at  $\sim 12:00$  PM (Fig. 5) show slightly higher concentrations overall and of particular note are the stairwells (on the far right and lower left in Fig. 5), which appear to serve as pathways for particles from the furnace floor to migrate upward into the electro-refining floor.

### Aerosol characterization

The particle number and size distribution measured at  $\sim 11:30$  AM by the FMPS during the pouring of molten feedstock into the anode molds show high numbers of nanoparticles (Fig. 6). ESP samples taken near the high-volume furnace during that time period, analyzed by TEM, show the typical

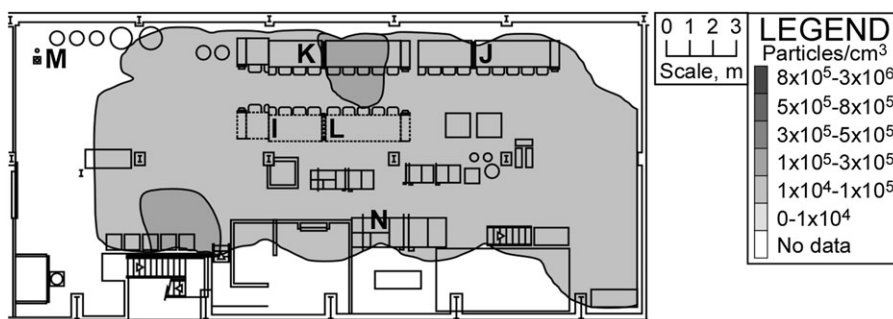


Fig. 4. Map of baseline particle number concentration on the electro-refining floor at 9:00 AM. Letters I–N are the locations for the area filters samples.

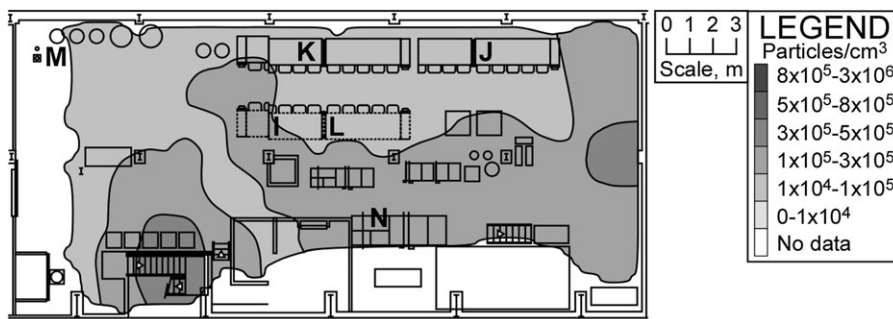


Fig. 5. Map of particle number concentration on the electro-refining floor at ~12:00 PM. Letters I–N are the locations for the area filters samples.

morphology of the particles (Fig. 7) and confirm the high number of nanoparticles measured by the FMPS. Analysis of these particles by EDS indicated that they are mainly metallic, including elements such as silver, lead, selenium, antimony, and zinc, as well as carbon and chlorine and that the relative amount of each element varied considerably from particle to particle. An example of an EDS spectrum for a typical particle collected near the high-volume furnace is shown in Fig. 8.

Similarly, FMPS data and ESP samples were collected during the pouring of refined silver ingots. The FMPS data (Fig. 6) show somewhat lower number concentrations than measured during the anode mold pour and again show that the particles are in the nanometer size range. TEM images from particles collected during pouring of refined silver show similar morphology and uniformity as the particles collected during the anode pouring process, as well as a high proportion of nanoparticles. The EDS data from individual particles, such as the spectrum in Fig. 9, show less variability than for particles generated during the anode pouring and also indicate higher levels of silver and less impurities.

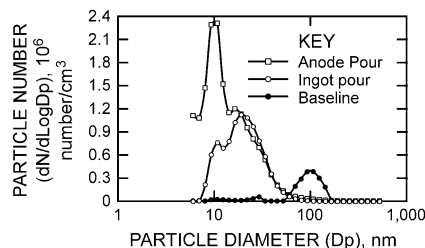
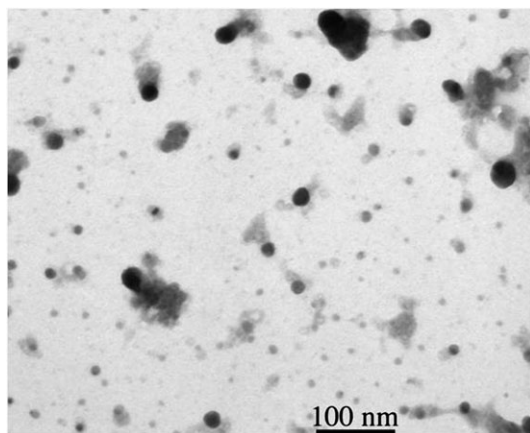
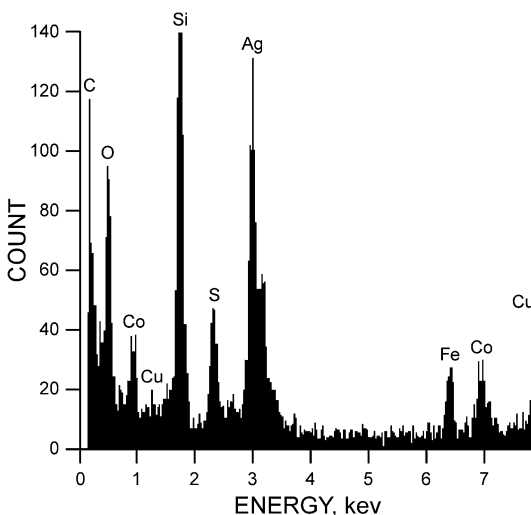


Fig. 6. Typical particle size distributions before and during the pouring of molten silver into anode molds and refined silver ingots.

Data from the two PDR photometers provide a valuable indicator of trends in approximate mass concentration in the workplace throughout the day (Fig. 10). The data in Table 2 show which events throughout the day resulted in increased levels of particulate matter in the air. The furnace floor monitor was near the high-volume furnace and thus shows very high values during the mold-warming task ~10:50 AM (due to use of propane torches) and during the anode pour ~11:20 AM.



**Fig. 7.** TEM image of particles collected during the pouring of molten silver into an anode mold.

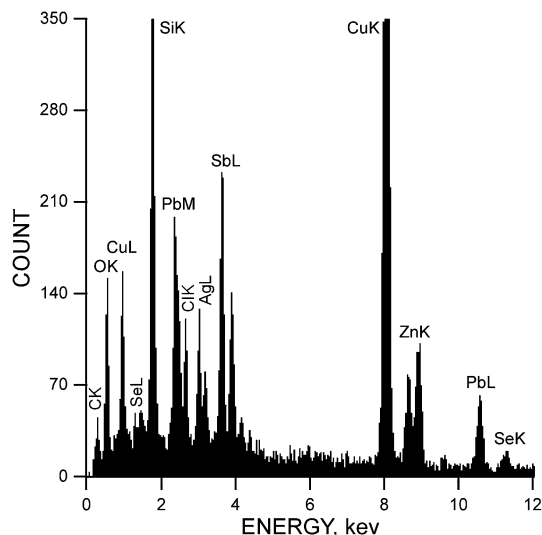


**Fig. 8.** EDS spectrum from a typical single particle collected near the high-volume furnace, showing contaminants including lead, zinc, and antimony. Note: This EDS spectrum is 'uncorrected' and the peaks from Cu, Si, and O must be assumed to be derived at least in part from the sample media and holder.

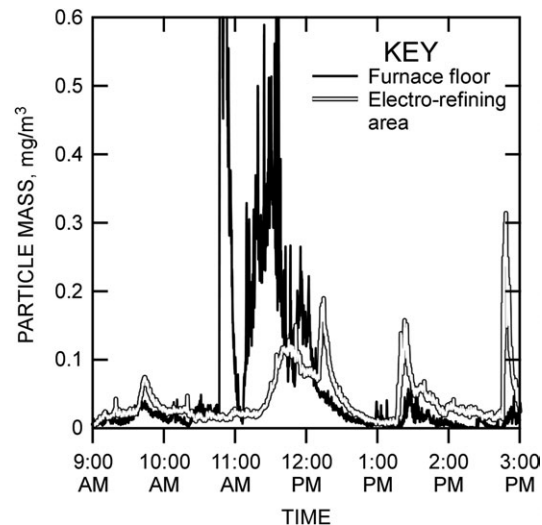
## DISCUSSION

### Filter samples

The results of filter sample analyses confirm that silver was the element of greatest concern. Airborne silver concentrations derived from all personal samples (ranging from 0.013 to 0.094 mg m<sup>-3</sup> total silver) as well as the area filter samples from the furnace floor (ranging from 0.013 to 0.039 mg m<sup>-3</sup>) exceeded the PEL for total silver, although none of



**Fig. 9.** EDS spectrum of silver particles collected near the low-volume furnace shows the lead and zinc have been removed but relatively low impurities of S, Fe, and Co remain. Note: This EDS spectrum is 'uncorrected' and the peaks from Cu, Si, and O must be assumed to be derived from the sample media and holder.



**Fig. 10** Light-scattering photometer data show particle mass concentration throughout the work shift on both floors.

the samples exceeded the ACGIH TLV of 0.1 mg m<sup>-3</sup> for total silver. The concentrations measured for other elements were well below both the PELs and TLVs. The total silver concentrations from the area filter samples on the electro-refining floor were consistently lower than for the samples on the furnace floor and only one area sample from the

Table 2. Events depicted by photometer particle mass concentration

Time	Event
10:00 AM	Feedstock in high-volume furnace began melting and a forklift began operating
10:50 AM	Furnace operator using propane torches to warm the molds
11:20 AM	Begin anode mold pour
12:15 PM	Near end of anode mold pour. A forklift also drove by the sampling station
1:30 PM	Startup of low-volume furnace. Warming up molds using propane torch
3:00 PM	Forklift activity

electro-refining floor (collected on a work bench where cells were cleaned and maintained; Location N in Figs 4 and 5) exceeded the PEL and none exceeded the TLV.

The two employees with the highest exposures to total silver (0.049 and 0.094 mg m<sup>-3</sup>) were not on the furnace floor where the highest ambient concentrations were found, but rather on the electro-refining floor. This suggests that these individuals performed tasks that entailed a localized high exposure to silver that was not detected by the area samples or during the mapping of the electro-refining floor. This type of task-related exposure is also supported by the personal exposure of the furnace floor operator (0.038 mg m<sup>-3</sup>) who also spent time in the chemistry laboratory. His exposure was the highest among the furnace floor employees, suggesting that he may have high exposure tasks in the chemistry laboratory or elsewhere in the refinery. The forklift worker on the furnace floor had exposures that were similar to the area samples collected from the furnace floor suggesting that the operation of the forklift does not increase the exposure to metal. The exposures of the furnace operators to total silver (0.018 and 0.029 mg m<sup>-3</sup>) were also greater than the PEL, which suggests the local ventilation systems on the two furnaces may not be adequately capturing the fumes.

The chemistry involved in electro-refining of the silver may be a potential source of soluble silver compounds, since soluble silver compounds have the potential to be mobilized via aerosolization of droplets from the liquid surfaces of the ion exchange cells. To investigate this, paired filter samples were collected above the electro-refining cells (Locations I-L in Figs 4 and 5). The first filter of each pair was analyzed for total silver, while the second was used to determine the soluble silver. Because of the low

temperature/low agitation operating conditions of the cells, the generation of silver aerosols was apparently low, thus all paired area samples were below the PEL for total silver. Although some soluble silver was evidently mobilized, it was still significantly less than the ACGIH TLV.

#### *Aerosol mapping and characterization*

The spatial maps of particle number concentration confirmed that the distribution of aerosols was initially low throughout the facility with a baseline level of particle concentration on the furnace floor in the range of  $\sim 5 \times 10^3$ – $5 \times 10^4$  particles cm<sup>-3</sup>. TEM/EDS data indicated that the background particles were mainly carbonaceous, assumedly from fugitive fossil fuel emissions.

The particle concentrations rose as the furnaces increased in temperature with a simultaneous decrease in the particle size (from a mean diameter of  $\sim 100$  nm for baseline particles to  $\sim 10$  nm near the furnace). Concentrations were highest in the region around the furnaces during mold pours, representing up to a 1000-fold increase in particle number over the baseline levels. Concentrations  $>10^6$  particles cm<sup>-3</sup> were measured regularly and are similar or slightly higher than levels measured previously in a foundry setting (Evans *et al.*, 2008). The high number of ‘nucleated metallic clusters’ (metal-rich nanoparticles with mean diameter of  $\sim 10$  nm) was often higher by a factor of two or three during the anode pours as compared to the pouring of ingots (Fig. 6), while both scenarios produced a ‘secondary mode’ of agglomerated nanoparticles with a mean diameter  $\sim 25$  nm. The TEM/EDS results indicated that most of these particles were low in carbon and high in metals, including silver and varying amounts of other metals such as lead, antimony, and zinc, suggesting they were derived primarily from the homogeneous nucleation of metal vapors. These particles differ considerably from those generated by combustion (mainly carbonaceous) or those resulting from metal vapors condensing onto existing particles, which result in more complex morphologies and composition (Miller *et al.*, 2007).

The baseline particle number concentration measured early in the day on the electro-refining floor was similar to the baseline on the furnace floor, but rose slowly over time. This may be a result of electro-refining activities or it may be the result of fugitive particles entering the electro-refining floor from the two furnaces below. The latter was supported by mapped data showing increased particle concentrations measured near the stairwells of the electro-refining floor relative to the rest of the room (Fig. 5)

suggesting the upward diffusion or convection of particles, even though the local ventilation systems were operating on the furnace floor.

This convection or diffusion of particles is further supported by the photometer data (Fig. 10). Work activities that produced increases in particle mass concentration on the furnace floor are sometimes reflected in the electro-refining floor data, with a short time lag. The best example of this occurred during the anode mold pour. The furnace floor photometer registered very high and quite erratic levels of airborne particulates during the molten metal pour, with peaks at ~11:20 and 11:55 AM. The electro-refining floor photometer measured similar peaks 15 minutes later, although less erratic and dampened due to the effects of diffusion and convection.

The FMPS data and TEM/EDS analysis of ESP samples collected during the pouring of molten silver confirm the generation of high numbers of metallic nanoparticles. The data show somewhat lower number concentrations during the pouring of refined silver (Fig. 3) than during the anode mold pour (Fig. 2), probably in part due to more effective ventilation around the low-volume furnace. The TEM/EDS data show that for both cases the particles are fairly uniform in morphology and have a proportionally high silver content, although the particles generated during the anode mold pour contained more contaminants than the refined silver particles.

## CONCLUSIONS

Worker exposure to airborne metals and nanoparticles was measured during refining of silver. The standard (filter sampling) approach provided measurements of worker exposure while the use of additional tools enhanced the results and provided a more complete picture of what was happening in the workplace. Enhancements included using real-time particle number concentration measurements along with subsequent spatial mapping to provide valuable information regarding particle generation and migration, while spot sampling and subsequent TEM/EDS analysis provided additional information on the particle morphology and elemental composition of the aerosols. Taken together, a comprehensive exposure assessment was completed and provided useful information for workplace exposure control decisions.

Results of the personal sampling revealed that all employee exposures exceeded the OSHA PEL for total silver, but not the ACGIH TLV.

The particle number concentration maps indicated that even though the furnaces had ventilation con-

trols in place, during the pouring of molten metal, airborne particle concentrations measured near the furnace were >1000 times higher than the baseline and FMPS data indicate a significant decrease in the mean particle size in that area. This suggests that the ventilation system was not capturing all the particles generated by the process and many were still traveling into the workplace from the furnaces.

The TEM/EDS data confirmed the FMPS result and also showed that the particles near the furnace were high in metal content. This not only increases the mass of metals to which the furnace workers are exposed but the smaller particle size also increases the bioavailability and thus the health risk (Ji *et al.*, 2007; Sung *et al.*, 2008). In this case, lower exposure to workers could potentially be achieved through ventilation redesign and modified operation of the furnaces.

To further investigate the potential for overexposures in such a workplace, time and motion studies could also be conducted, especially on electro-refining floor and chemistry lab personnel who had the highest exposures to silver. That analysis would help detail exactly where employees conduct various activities during a work shift. Combining that information with additional detailed mapping of particle concentrations would yield valuable insight into sources of worker exposure. Information from these alternative methods, as well as personal and ambient exposure data and real-time measurements (such as with a photometer), may help identify the most significant exposure sources where additional controls are needed.

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