CHAPTER 7
METAL DUSTS, FUMES AND MISTS

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I. Introduction

Metals, alloys, and compounds are found in a wide variety of mining operations. Milling, welding, and plating are examples of mechanical, thermal or electrochemical processes that can alter the size, state or chemistry of a metal or its compounds. Welding produces fumes; grinding and milling produce dusts and electrolytic refining processes create mists containing soluble metallic compounds. Inhalation is the most common route of entry for metal dusts, fumes, and mists. Exposures to metals are evaluated as the mass of a metal or its compound in a known volume of air. The analytic methods used allow multiple metals to be identified from one sample.

Acute or chronic exposure to hazardous metals and their compounds can cause injury or illness. For example:

1. Metal fume fever and pneumonitis are caused by acute exposure to high concentrations of metal fumes (such as zinc, magnesium, and their oxides). Symptoms, usually fever and chills, appear from 4 to 12 hours after exposure. Persons usually recover within one to two days, but symptoms can recur with repeated exposure. Over-exposure to cadmium or cadmium oxide fume can result in fatal pulmonary edema a day after exposure.

2. Pneumoconiosis is a “dust disease of the lungs” caused by the accumulation of mineral or metallic dust particles in the lungs due to chronic exposure. This can result in decreased lung function, an increase in the demand placed on the cardiovascular system, and eventual heart failure. The accumulations are identified as “shadows” on the lungs that can be seen in chest radiographs. Some of the pneumoconioses are benign, while others may lead to fibrosis (scarring) of the lung and continue to spread after exposure to the hazard ends. Some metal exposures can cause cancer (arsenic, beryllium, cadmium, chromates, nickel, and lead). Exposure to beryllium and its alloys may lead to a progressive lung disease know as berylliosis.

3. Systemic poisoning is the damage to organs (such as kidneys or liver) or organ systems (such as the reproductive, urinary, circulatory, respiratory, or central nervous systems) when a toxic agent enters the body. Inhalation

is the most common route of entry for metal fumes and dusts. Bone cancer, blood cancer (leukemia), kidney failure, or heart failure can result. Because the early symptoms of metal poisoning (e.g., blurred vision, headache, fatigue, delirium, diarrhea, and chest pains) are often attributed to other causes, misdiagnosis can occur.

II. Definitions

Dust - fine, dry, solid particles of earth or metal. Dust particles can be produced and suspended in the air by cutting, drilling, crushing, grinding, screening, loading, etc. Dusts can be inhaled and ingested. Sources of metal dusts are primarily associated with metal ore mines and mills. Equipment operators and cleanup personnel may experience a higher risk of dust overexposure near “concentrate piles” or in processing plants where minerals are processed, transported, handled or loaded.

Elemental Analysis - typically, a profile performed by the MSHA Laboratory to determine the amount of 14 elemental metals and metalloids in fumes and 8 metals in dust samples. Refer to Section V.B.2.d. for soluble salt analysis. An elemental analysis can be requested for one or any combination of the 14 basic elements. The results are used to determine compliance with the respective limits for oxides or compounds listed or referenced in the ***TLVs® Threshold Limit Values for Chemical Substances in Workroom Air Adopted by the ACGIH for 1973***.

Elemental Metal - the basic form of a metal, uncombined (as a compound) with any other chemical element. For example, elemental lead is pure lead, as opposed to lead oxide (in welding fumes) or lead sulfide (lead ore dust). Of the 92 basic natural elements, 53 are metals. Thirty-six of these metals have enforceable TLVs®.

Fumes - airborne particles formed when a metal, which is solid at room temperature, is melted, vaporizes into the atmosphere, and then condenses to a solid. Fumes usually assume rounded or smooth, irregular shapes, generally less than one micron in size, but sometimes they join together to form larger particles. Fumes are produced by welding and oxy-fuel torch cutting operations, in furnaces producing molten metal and in small assay lab furnaces.

Metalloid - chemical elements with both metallic and non-metallic properties that may have toxic systemic effects on the human body. Metalloids can be found in dusts and fumes. Some metalloids found in the mining industry are boron, tellurium (telluride), arsenic, and antimony.

Mists – suspended liquid droplets generated from the mechanical disruption of a liquid via agitation or atomization. These droplets can be formed from liquids containing soluble forms of metals.

Stoichiometric Multiplier or Gravimetric Factor - a number used in an exposure calculation when the standard in the ***TLVs® Threshold Limit Values for Chemical Substances in Workroom Air Adopted by the ACGIH for 1973*** is listed as a metal oxide and when the analytical method is not specific for the compound. The stoichiometric multiplier is used to compensate for the additional weight of oxygen which is not included in the metal analysis (see Section VIII). The MSHA laboratory will include the appropriate adjustments in the exposure report.

Hazards Associated with Welding and Cutting - the following factors can affect the type and toxicity of hazards:

1. Type of material - iron or steel can produce iron oxide, nickel compounds, and chromium trioxide fumes. Stainless steel can produce manganese and other toxic fumes. Alloys may produce copper, zinc, and tin oxide fumes.

2. Coatings - on base metals will be vaporized during welding or torch cutting. Plated or galvanized metal may release cadmium or zinc oxide fumes. Metals painted with lead-based or older latex paints may release lead or mercury fumes. Metals with residues of chlorinated-chemicals like solvents or metals with plastic coverings can release hydrogen chloride into the air, an acid gas which becomes hydrochloric acid if it contacts the moist linings of one's respiratory system.

3. Welding rods and electrodes, fluxes, and fillers - release metal fumes into the atmosphere. Welding and hard-facing rods and electrodes typically contain chromium, copper, iron, manganese, molybdenum, nickel and titanium. Take titanium samples on a separate filter. Many welding rods and electrodes contain fluoride flux which can be released in toxic forms. Most filler compounds contain silica or calcium which may become free silica or calcium oxide.

4. Gases - commonly produced during welding include carbon monoxide, carbon dioxide, ozone, nitrogen oxides, phosgene (from the decomposition of chlorinated hydrocarbons), and hydrogen chloride. Inert shielding gases can, without proper ventilation, displace breathing air.

III. Exposure Limits

The full-shift threshold limit values (TLV®) and short-term exposure limits (STEL) for metals and metalloids are listed or referenced in the ***TLVs® Threshold Limit Values for Chemical Substances in Workroom Air Adopted by the ACGIH for 1973*** and are incorporated by reference in MSHA standards for Metal and Nonmetal mines. Refer to chapter 3, Contaminant Index. The MSHA Laboratory will provide the appropriate TLV® or STEL for the form of the metal that was sampled and analyzed.

IV. Sampling Equipment

A. Filter Cassette

Use mixed cellulose ester (MCE), 37 mm in diameter, 0.8 micron pore size filter cassettes for all metal fumes and dusts, including welding fumes. See V.B.1. below. Aluminum and titanium require different sample preparation from the other 14 metals sampled this way and should be submitted with a separate MCE filter for each analysis required. Chromic acid and chromates require a separate sample because the analytical method requires a different filter material. See V.B.2., "Other-Special," for a description of PVC filters for chromates and chromic acid.

B. Personal Sampling Pump

Any sampling pump may be used that can maintain the specified flow rate (see Section VI.A).

V. Sampling Strategy

A. Duration of Samples

1. Full-Shift Samples

Full-shift sampling should be used when miners will be exposed to metal dusts or fumes during all or most of their workshift. In order to determine if the TLVs® have been exceeded, sample the miner's entire workshift, regardless of the number of hours worked. [Refer to Chapter 2. III. A. 1.]

2. Short-Term Samples

Short-term samples can be taken independently or in conjunction with full-shift samples to determine if the short-term exposure limits (STEL) or ceiling limits have been exceeded during suspected periods of peak exposure. When monitoring for short-term exposure limits, refer to the sampling times listed in Chapter 3. In general, when sampling welding fumes, the sample duration should be 30 minutes to encompass all of the specified time periods for the 14-element profile. When sampling a mixture of similar metallic contaminant dusts or fumes, the sampling duration should correspond to the contaminant with the longest STEL time period. However, if sampling for one specific contaminant, the duration should correspond to the listed time for the respective STEL. This can be accomplished by:

a. Taking a sample in the miner’s breathing zone using the sampling procedure described in section VI;

b. Taking an additional short term sample during a full shift sample to determine if short term exposure limits or ceiling limits for a specific contaminant are exceeded;

c. Interrupting the full-shift sample to conduct short term sampling. This method requires taking consecutive samples. Each sampling period requires a separate cassette, and the contaminant amounts on each cassette must be added to obtain the full-shift exposure for each contaminant. (For example, if two short-term samples were taken in addition to the full shift sample, the shift weight of the contaminant equals the weight on the full-shift filter plus the weight on the first short-term filter plus the weight on the second short-term filter.) [Refer to Chapter 2. III. A. 2.]

B. Laboratory Analysis

1. Elemental

An elemental analysis can be requested for one, or any combination of the following metals (unless specified, the analysis will include all 14):

Arsenic (As)	Lead (Pb)
Beryllium (Be)	Magnesium (Mg)
Cadmium (Cd)	Manganese (Mn)
*Chromium (Cr)	Molybdenum (Mo)
Cobalt (Co)	Nickel (Ni)
Copper (Cu)	Vanadium (V)
Iron (Fe)	Zinc (Zn)

* Note: Chromium results from elemental analysis with ICP can only be applied to the TLVs® for contaminant codes 545 and 547:

- Chromium metal;
- Soluble chromic and chromous salts - chrome, chromium phosphate, chromium carbonate, and chromium acetate; and
- Insoluble chromium salts.

When the lab performs an elemental analysis on a welding or metal fume sample, chromium is reported as the metal only (i.e., contaminant code 547), not the oxide form. There is another more specific method available for determining the oxidized form of chromium. If exposure to hexavalent chromium is suspected, arrangements for expedited sample analyses must be made prior to sampling. Sample flow rate: usually 1.7 Lpm for up to 9 hours. Reference Chapter 3 and NIOSH Method 7600.

2. Other-Special

a. During certain welding operations (*e.g.*, on stainless steel), and in some ore dusts, chromium may occur in the especially hazardous "hexavalent" form (CrVI). When chromium VI, chromic acid, or chromates are present or suspected, take a separate sample using a pre-weighed mineral-dust filter cassette (37 mm diameter, polyvinyl chloride (PVC), 5 micron (µm) pore size). **Note: Remove the filter from cassette and place filter into a glass vial after sampling. Discard the plastic cassette. Since the sample will be stable for only two weeks, it must be shipped without delay (overnight) to the MSHA Laboratory (see Chapter 3).** Notify the MSHA Laboratory in advance of your need to sample for hexavalent chromium.

b. The MSHA Laboratory routinely processes samples for other metals, such as silver, barium, calcium, mercury, and sodium. These must be sampled individually using a separate MCE filter and blank. Contact the MSHA Laboratory for handling and shipping requirements for these samples.

c. If it is necessary to sample for additional metals or metalloids, contact the MSHA Laboratory for sampling and handling guidance.

d. Analyzing for soluble metal salts including Cd, Cr, Fe and Mo requires a different sample preparation procedure than that routinely performed for welding fumes. Please specify on the RLA form if an analysis for soluble metal salts is needed. If insoluble metals are also required, take two side-by-side samples.

VI. Sampling Procedure

A. Pre-survey Calibration of the Sampling Pump

Calibrate the personal sampling pumps for fume and elemental dust sampling in accordance with the policy and procedures contained in Chapter 4. The recommended flow rate for full-shift and short-term sampling is 1.7 Lpm. Acceptable sampling flow rate ranges are listed in Chapter 3.

B. Prepare Blank Filter

A blank filter cassette(s) is submitted to determine contamination of the cassette from sample handling, storage, and shipping. Prepare one blank filter for each type of analysis desired. For example, “elemental” (all 14 metals listed in Section V.B.1) analysis requires one blank and “silver” would require another. In addition, separate blanks <u>must</u> be submitted for each set or shift sampled. Blanks must come from the same (lot) box of cassettes used for the exposure sampling period.

1. Remove the inlet and outlet plugs and quickly replace them. This should be done at the mine site, preferably at the sampling area.

2. Number or uniquely identify the cassette. Treat the blank filter the same as the exposed filters.

3. At the end of the shift, place a Sample Seal label (MSHA Form 4000-30) on the filter cassette. Date, sign, and mark "BLANK" on the sample seal. Record all blank filter information in the Health Field Notes.

C. Assemble the Sampling Train

1. Number or uniquely identify the cassette. This will be the sample number noted on the Request for Laboratory Analysis form.

2. Attach the cassette to the sampling pump.

a. Remove the inlet and the outlet plugs of the cassette (to take a "closed-face" sample). Place the plugs in a clean, convenient location (*e.g.*, in a plastic bag) for future re-use.

b. Insert the coupler in the end of the sampling hose into the outlet side of the cassette. Then attach the other end of this hose to the sampling pump inlet.

c. Make sure that all fittings are tight and that the cassette is secured in the lapel holder (if used).

D. Attach the Sampling Train to Miner

1. Attach the sampling pump and sampling train to the miner so that it will not create a safety hazard to him or her or anyone else while performing normal activities. If the miner is not wearing a shirt or belt, the inspector should provide a belt or vest to facilitate sampling.

2. Attach the closed-faced filter cassette assembly, filter facing downward, and in the miner's breathing zone (see Figure 7-1). For welding fume samples, the breathing zone of a welder wearing a welding hood is considered to be under the hood when the face shield is in the down position (see Figure 7-2). Note: Helmet sampling adaptors (pre-formed tubing with Velcro attachments) for welding fume sampling are available from several manufacturers. Contact your District Office to coordinate this purchase.

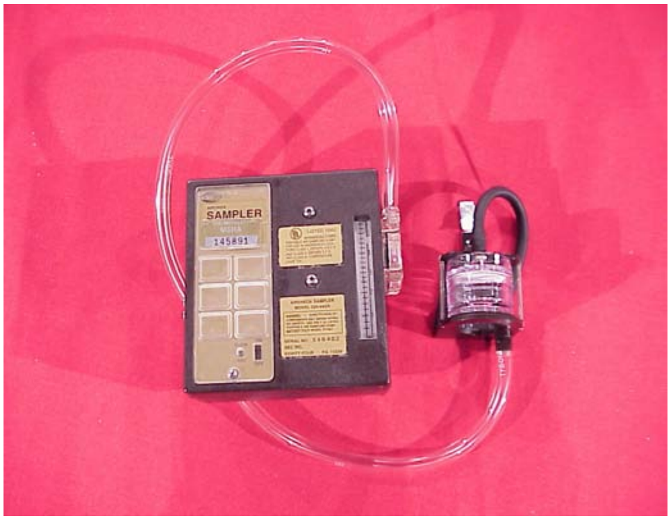

Figure 7-1. Elemental Dust Sampling Train

Figure 7-2. Welding Fume Sampling Train

E. Instructions to the Miner

1. Explain to the miner what you are doing, what the sampling device does, and the reason for the sampling (i.e., the hazard). If available, issue a Miner Health Hazard Information Sheet or Card.

2. Instruct the miner not to remove the sampling pump or sampling train at any time or cover the cassette inlet with a coat or anything else. If the miner must leave the mine property during the shift, the inspector should remove the sampling train and turn the sampling pump off. Sampling should continue once the miner returns.

3. Instruct the miner not to bump, drop, abuse, or tamper with the sampling pump or sampling train.

4. Emphasize the need for the miner to continue to work in a routine manner and report to you any unusual occurrences during the sampling period.

5. Inform the miner when and where the sampler will be removed and that you will be checking the equipment throughout the shift.

F. Collect the Sample

1. Turn on the sampling pump and replace the cover plate.

2. When the sampling train has been attached, record in the Health Field Notes (refer to Chapter 21, Section V):

a. Time the sampling pump was started;

b. Pump and filter cassette identification numbers;

c. Miner's name, job title, and work location(s);

d. Shift hours per day and days per week worked;

e. Any respirator worn or expected to be worn (brand, model, type of filters); and

f. Whether an acceptable respiratory protection program exists (see Chapter 16 for criteria for evaluating respiratory protection program).

3. During each full-shift sample, the inspector must observe the miner being sampled as frequently as is necessary to determine that a representative sample is being conducted of the normal activities. Check the sampling pump and sampling train to make sure that the sampling pump is operating properly, and to make sure the tubing and connections are not leaking. Do not adjust the flow rate at any time while sampling. Record what tasks the miner has performed in the time between subsequent checks, so that the completed Health Field Notes will describe the miner's full work shift. This requirement does not necessarily preclude the inspector from doing other inspection work while sampling.

4. Evaluate dust and fume conditions. Significant amounts of dust and fume in the work environment may require the changing of filter cassettes to keep them from becoming overloaded.

Filter overloading may occur when collecting personal samples for metals during certain processes (e.g., charging furnaces, pouring ingots, sanding, grinding, etc.) because of the short-term generation of large volumes of particulate matter. To prevent overloading (as evidenced by any loose particulate on the filter), use consecutive sampling with shorter sampling periods.

5. Throughout the shift, record all other pertinent information in the Health Field Notes:

a. Times that the sampling train was checked and condition of sampling equipment. If the sampling pump needs to be changed out, stopped, or restarted for any reason, record the times involved;

b. If consecutive samples were taken, record the number of any additional cassettes used during sampling period;

c. Activity of miner, equipment operating in the area, and approximate time spent at each activity;

d. General description of controls in use and whether or not they seem adequate;

e. Potential sources of exposure, a general description of these sources, number of persons affected, and possible additional control measures;

f. Any other samples taken and the results, if available (*e.g.*, noise, detector tubes, organic vapor badges); and

g. Environmental conditions (such as wind conditions, temperature, humidity, etc.).

6. Collect the sampling train from the miner.

a. <u>Turn</u> <u>off</u> the sampling pump. Record the time the pump was turned off.

b. <u>Carefully</u> remove the sampling train.

c. Uncouple the filter cassette from the sampling train and replace the cassette plugs. Place a sample seal on the filter cassette. Date and sign the sample seal.

VII. Post-Inspection Procedures

A. Review Health Field Notes

Check that you have recorded all necessary information in the Health Field Notes (MSHA 4000-31).

B. Post-Survey Calibration of Sampling Pump

Check the sampling pump calibration using the procedures in Chapter 4.

C. Transport Samples for Analysis

1. Complete the Request for Laboratory Analysis (MSHA Form 4000-29) for air samples and blanks (refer to Chapter 21, Section VII).

- <u>Item No. 15 (sample type)</u> - designate “MD” for metal dust sample, “W” for welding fume sample, “MF” for other metal fume sample, or “CB” for blank cassettes.

- <u>Item No. 16 (analysis desired)</u> - identify analysis desired. For example; “elemental 14,” “chromates,” “silver,” or “calcium oxide.”

2. Ship the Request for Laboratory Analysis Form(s) and samples to the MSHA Laboratory. (Keep a copy for yourself.) Filter cassettes and blanks can be shipped together in the same container if space allows.

VIII. Documentation and Recordkeeping

A. Compliance Determination

Results will be received from the Laboratory with exposure concentrations calculated using the appropriate stoichiometric factor and applicable TLV®/STEL on an “Analytical Report.” A value greater than 1.0 in the C/TLV®*EF column indicates a citable violation. Complete the Action Code and Citation number on the accompanying PEDS.

1. Stoichiometric Multiplier (S.M.) (Gravimetric Factor)

The analytical method is specific for the element to be determined and does not distinguish different compounds. To calculate a compound value, a gravimetric factor is applied. When the standard in the ***TLVs® Threshold Limit Values for Chemical Substances in Workroom Air Adopted by the ACGIH for 1973*** is listed as a metal oxide, a stoichiometric multiplier (S.M.) is used in the exposure calculation for fume samples. The stoichiometric multiplier is used to compensate for the additional weight of the oxygen which is not included in the metal analysis. The metal weight is multiplied by the stoichiometric multiplier to obtain the mass of the oxide. The stoichiometric multipliers used by the MSHA Laboratory for metal oxides with an applicable TLV® are listed below.

Contaminant as Listed in 1973 TLV® Booklet	Compound for Which the TLV® is Calculated	Stoichiometric Multiplier
Alundum (Aluminum Oxide)	Al_2O_3	1.889
Iron Oxide Fume	Fe_2O_3	1.430
Magnesium Oxide Fume	MgO	1.658
Titanium Dioxide	TiO_2	1.668
Zinc Oxide Fume	ZnO	1.245
Calcium Oxide	CaO	1.399

Note: When a metal compound does not have a specific TLV®, a stoichiometric multiplier is not used in the exposure calculation; for example, lead sulfide does not have a specific TLV®, but is regulated as “lead, inorganic, fumes and dusts.” If it is present in a sample, a stoichiometric multiplier would not be applied. In this case, the Laboratory would report the concentration as elemental lead, not the compound. Therefore, if the concentration of elemental lead exceeded the TLV® or STEL, an overexposure occurred.

2. Calculations

Exposure concentrations are calculated using the following formulae. Determine compliance by comparing calculated exposure concentrations with respective exposure limits. The MSHA Laboratory will calculate personal exposure sample result concentrations in an “Analytical Report” mailed back to the sample collector.

a. Full-Shift Sample - Shift-Weighted Average (SWA)

Calculate full-shift exposure using the following formula:

$$\frac{\text{wt. of contaminant (mg)} \times \text{S.M. (when applicable)}}{\text{Flow rate (Lpm)} \times 480 \text{ (min)} \times 0.001 \text{ (m}^3\text{/L)}} = \text{SWA in mg/m}^3$$

where: S.M. = Stoichiometric Multiplier.

(If the full-shift sample was started and then interrupted to take consecutive short-term samples, the weight of contaminant is the sum of the contaminant on each filter.)

b. Short-Term Sample - Time-Weighted Average (TWA)

Calculate the concentration for each contaminant from the following:

$$\frac{\text{wt. of contaminant (mg)} \times \text{S.M. (when applicable)}}{\text{Flow rate (Lpm)} \times \text{actual sampling time (min)} \times 0.001 \text{ (m}^3\text{/L)}} = \text{TWA in mg/m}^3$$

where: S.M. = Stoichiometric Multiplier.

c. Additive Effects

See Chapter 2 for a discussion of additive effects and calculation examples.

d. Error Factors

The error factors for metal fume and dust sampling and analysis will be supplied by the MSHA Laboratory.

B. Report Writing

1. Inspection reports should include a copy of the Health Field Notes, the Request for Laboratory Analysis forms, Laboratory Analytical Reports, the completed Personal Exposure Data Summary (PEDS), calculation worksheets, citation/orders, and any other supplemental information collected during the inspection.

2. When completing the PEDS for mists by hand (refer to Chapter 21, Section VIII), be sure that the concentration and exposure limit units of measurement are the same as those listed for the contaminant code (refer to Chapter 3).