Industrial Hygiene Air Analysis by Atomic Absorption: Sample Collection and Handling for Trace Metal Particulates

Application Note

Atomic Absorption

Author

Alan J. Stratton

Introduction

Atomic Absorption (AA) is an established analytical technique for the industrial hygiene (IH) evaluation of worker exposure to numerous airborne particulates (see Table 1) in a variety of industrial environments. Like all analytical techniques, the procedure begins with sample collection and preparation. Unlike most other analyses, however, the analyst frequently plans the sampling procedure with an industrial hygienist.

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Regulatory Agency Requirements

Analysts confronted with IH analyses should first determine whether any federal, state or local regulations require use of specific sampling and analytical methodology. In the absence of any official procedure, the monitoring information wanted may often warrant utilization of methods recommended by some regulatory agency, for example, NIOSH* in the NIOSH Manual of Analytical Methods (NMAM). IH analysts may also select or develop any method considered feasible for compliance monitoring. However, since regulatory agencies can mandate specific analytical procedures at any time, analysts and others responsible for IH evaluations should establish sources of information to keep informed of current regulatory developments.

Criteria for Sampling Procedure

The sampling procedure should be based on the following two criteria. First, what is the purpose of sampling? Second, what property of the sample requires measurement? Since the analytical method of interest here is AA, the quantity of specific elements present in the sample is the property to be measured. However, the main purpose of industrial hygiene sampling is to monitor and evaluate the health risk from employee exposure to airborne chemical contaminants. This usually means determining the concentration of contaminants in the air inhaled by workers in various industrial environments. For AA measurements, this involves extrapolation of a measured elemental concentration in a chemically treated sample preparation to the elemental or molecular concentration of a contaminant in a measured volume of air. As a rule, the analyst is mainly concerned with the AA measurement and the industrial hygienist with the health risk assessment. Their concerns overlap, however, when planning the optimum sampling procedure.

Two general sample types are utilized for IH evaluations of worker exposure to airborne contaminants: area samples and personal samples. Contaminant concentrations at a selected work site or specific location within the work site are indicated by an area sample. This stationary sample enables determination of background levels of airborne contaminants, which often vary from one location or operation in a work site to another. The efficiency of control equipment (ventilation systems) can also be evaluated using area samples.

Table 1. OSHA PEL Values for Contaminants Analyzed by AA*

Substance	PEL
Antimony and compounds, (as Sb)	0.5
Arsenic and compounds (as As)	0.010 (inorganic) 0.5 (organic)
Barium, soluble compounds	0.5
Beryllium and compounds	0.002
Cadmium, dust	0.2
Cadmium, fume	0.1
Calcium oxide	5
Chromium, metal and insoluble salts	1
Chromium, soluble chromic, chromous salts (as Cr)	0.5
t–Butyl chromate (as $Cr0_3$)	0.1
Cobalt, metal, fume and dust	0.1
Copper, dust and mist	1
Copper, fume	0.1
Ferrovanadium dust	1
Hafnium	0.5
Iron oxide fume	10
Lead, metal, inorganic compounds and organic soaps	.050
Lithium hydride	0.025
Magnesium oxide fume	15
Manganese	5
Mercury	0.1
Organo (alkyl) mercury	0.01
Molybdenum, insoluble compounds	15
Molybdenum, soluble compounds	5
Nickel, metal and soluble compounds (as Ni)	1
Platinum, soluble salts (as Pt)	0.002
Rhodium, metal fume and dust (as Rh)	0.1
Rhodium, soluble salts	0.001
Selenium compounds (as Se)	0.2
Silver, metal and soluble compounds	0.01
Tantalum	5
Tellurium	0.1
Thallium, soluble compounds (as Tl)	0.1
Tin, inorganic compounds except oxides	2
Tin, organic compounds	0.1
Titanium dioxide	15
Vanadium, V_20_5 dust	0.5
Vanadium, V_20_5 fume	0.1
Yttrium	1
Zinc chloride fume	1
Zinc oxide fume	5
Zirconium compounds (as Zr)	5

* Permissable exposure limits (in milligrams per cubic meter of air) as of June 1979.

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* Abbreviations for IH organizations and exposure limits are defined in AA-002 of this series

The other general IH sample type is the personal sample. It is collected only in the "breathing zone", generally defined as a sphere approximately two feet in diameter surrounding a worker's head. Consequently, this sample best indicates the actual amount of contaminant inhaled by an individual worker who is mobile throughout the work site. OSHA specifies that personal samples be collected for monitoring the time-weighted average (TWA) exposure of workers to certain chemical contaminants (for example, lead and arsenic).

Particulates

Airborne chemical contaminants exist in the form of gases, vapors, or particulates (shortened form for particulate matter). AA analyses generally involve only particulates, the generic term for any airborne suspension of liquid or solid particles which can be further categorized as a fume, mist, smoke or dust. Occasionally, the term "aerosols" is used to refer to particulates.

Condensation in air of a molten substance (usually a metal) forms solid airborne particles collectively called a primary fume. Direct dispersion from a bulk source or re-dispersion of a previously settled primary fume creates a secondary fume. Although primary fume particles are usually finer than secondary ones, both types have irregular shapes. Fumes are usually generated by high heat industrial operations such as metal welding and hot rolling.

Smoke consists of very fine particles and usually results from incomplete combustion. Smoke particles are usually organic although some smokes contain mineral residues.

Mist particles are spherical airborne liquid droplets created by bubbling, boiling, spraying, of a liquid or by condensation from air supersaturated with a vapor. Mists may also contain substances analyzed by AA (for example, elements dissolved as ions).

Primary airborne dust results from crushing, grinding, and other similar industrial operations which disperse solid particles into the air. Re-dispersion of previously settled primary airborne dust or dispersion of fine powder from a bulk source constitutes secondary airborne dust. So-called "respirable dust" is comprised of particles 0.5 to 1.0 microns in mean diameter, a size, which is most likely to lodge in the human lung. Dusts are the most common form of particulate matter analyzed by AA.

Sampling Equipment

Sampling Train

Collection of either area or personal samples typically involves utilization of a sampling train comprised of an air pump, filter, and filter holder. Most pumps include an airflow indicator and a valve to control the volume of air sampled. If a "respirable dust" sample is required, a particle size separation device (for example, an elutriator or a cyclone) placed at the front of the sampling train eliminates coarser particles before sample collection on the filter.

Personal Samples

The overwhelming majority of IH samples analyzed by AA are personal samples. As recommended by NIOSH, these are collected utilizing a portable personal sampling pump. Compact, lightweight, and powered by rechargeable batteries, it is usually attached to a worker's belt where it can be comfortably carried without hampering job performance. The pump is connected by a suitable length of tubing to a standard 2-piece or 3-piece plastic filter holder called a cassette or monitor (see Figure 1). The cassette houses a mixed cellulose ester (MCE) membrane filter and has two small plugs, one at either face, which are removed during the sampling period. The membrane filters typically are 37 millimeters in diameter, contain 0.8 or 0.45 micrometer pores, and are placed against a backing pad or screen for support inside the cassette. The loaded cassette is usually clipped face downward (towards the floor) onto a worker's collar during the sampling period required by OSHA or dictated by the analytical sensitivity of the AA technique used for the measurement. For large-particle industry environments, attachment of a particle separator downstream of the filter cassette may also be required.

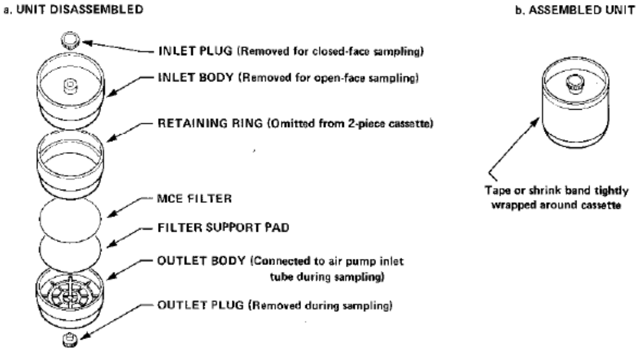

Figure 1. Filter cassette.

Area Samples

Area samples can also be collected with a portable personal sampling train by placing it in a stationary position in the work zone. Frequently, however, a stationary, high-volume air pump may replace the portable pump, especially if a larger sample is required.

Sample Collection Modes

Two modes of sample collection are possible with the standard cassette filter holders. If the clear-faced inlet body of a 3-piece cassette is removed, the MCE filter is completely exposed for "open-face" sampling which allows particulates to collect over the entire membrane filter surface. The center-retaining ring of a 3-piece cassette holds the filter and filter support pad securely in place when the inlet body is removed. A 2-piece cassette lacks this center section. When only the inlet plug is removed from the inlet body, the "closed-face" sampling mode is enabled which causes particulate build-up mainly on the center portion of the membrane. Either a full 3-piece or a 2-piece cassette can be used for closed-face sampling. All filter cassettes should be wrapped around their circumference with tape or cellulose shrink bands to prevent leakage during sampling and handling.

Upon completion of the sampling period, the end plugs and/or inlet body are replaced. The entire cassette, including the filter containing the collected particulate matter, should then be delivered as a unit to the analytical laboratory. There, laboratory personnel can carefully remove the fragile MCE filter just prior to its preparation for the AA analysis.

Air Pump Calibration

The units for PELs, TLVs, and other worker exposure limits are usually in micrograms or milligrams of contaminant per cubic meter of air. The volume of air sampled, therefore, is a primary parameter to be determined. Most pumps have rotameters, which can range in accuracy from ± 5% to ± 25%, to indicate the volume of air sampled per unit time, typically in cubic feet or liters per minute. Furthermore, pump performance varies with time due to corrosion, dirt accumulation, worn parts, etc. Consequently, air pumps must be calibrated at regular intervals. Although many different calibration devices are available, a soap-film flow meter is among the simplest, most accurate, and commonly utilized. Basically, a cylindrical air displacement meter, it indicates pump flow rate by measurement of the time required for a soap bubble or film to pass through a graduated volumetric cylinder which is connected to an operating air pump filled with a cassette and filter. After calibration and sampling, multiplying the calibrated flow rate (in liters per minute) times the sampling time (in minutes) gives the volume (in liters) of air sampled. Dividing by 1000 then gives the volume in cubic meters. The formula for this calculation is:

$$V = \frac{rt}{1000} \tag{1}$$

where

V = volume of air sampled in cubic meters
r = numerical value of air pump flow rate
(calibrated in liters per minute)
t = sampling time in minutes

Many personal sampling pumps have constant flow devices which automatically maintain a constant air flow rate during sampling. Pumps not equipped with this feature usually have rotameters to indicate flow rates. When initial and final flow rates differ significantly, NIOSH recommends using the average flow rate, *r*, to calculate the volume of air sampled as indicated by the following formula:

where

$$r = \frac{i + f}{2} \tag{2}$$

i = initial pump flow rate
f = final pump flow rate

This flow rate value can then be used for the air volume calculation above in formula 1.

Determinations of particulate concentrations generally do not require temperature and pressure considerations (as gaseous contaminants do) if the pump calibration is performed at the ambient conditions of the air to be sampled. However, when field sampling conditions differ significantly from calibration conditions, NIOSH recommends use of a special formula (see Ref. 4, Vol. 5). This compensates only for the effect of air density during calibration of the rotameter type pump.

Representative Samples

Valid IH assessment depends upon collection of representative samples which represent actual worker exposure to the contaminants in the work environment. To determine this, it is necessary to know when, where, whom, how long, and how often to sample. The answers to these questions depend upon the analytical techniques employed by the laboratory as well as the environmental conditions, operational procedures, and personnel involved in the workplace.

Instantaneous or "Grab" Sampling

Sampling for any time period less than five minutes is referred to as instantaneous or "grab" sampling. Such a short sampling duration only represents the momentary contaminant concentration and is, therefore, generally not utilized for TWA exposures. Grab samples are suitable, however, for determining airborne contaminant concentrations during several short phases of a cyclic operation. Consecutive samples indicate the variation of concentration with time. Since the quantity of material collected is generally very small, carbon rod or vapor generation techniques are usually necessary for the AA analysis. Grab samples collected with Agilent's air microsampler are analyzed directly with the carbon rod atomizer.

Integrated Sampling

Integrated sampling or sampling for more than five minutes is often required by OSHA. The term is generally used, however, to describe the collection of gaseous contaminants by absorption in liquid solution or absorption on a solid. Nevertheless, the concept of sampling over a relatively long period of time to establish a TWA exposure does apply to the process of particulate sampling followed by AA analysis. Since a longer sampling time yields more particulate matter on an MCE filter, integrated samples may also be collected to overcome the problem of insufficient sensitivity to low particulate concentrations.

Minimum Sample Volume

How long to sample is a major question analysts help to answer because the answer depends fundamentally on the accuracy, precision and analytical sensitivity of the analytical technique. However, contaminant concentrations may fluctuate during a workshift or vary in different locations or during different operations in the workplace. Consequently, the analyst determines the minimum sample volume necessary for a satisfactory analysis and the industrial hygienist can then decide if a longer sampling time is necessary to monitor fluctuations of the contaminant concentration in the air sampled.

The AA analyst can easily determine the minimum sample volume required to obtain a reasonable absorbance using the characteristic concentration, for example the concentration of an element which produces an absorbance of 0.0044. For example, consider the determination of arsenic in air using the vapor generation technique. The characteristic concentration, c, for arsenic is 0.0002 pg/mL. Typically, the filter preparation for air analysis involves dilution to some volume. This is often 100 mL. Hence, 0.0002 μg/mL × 100 mL = 0.02 μg of arsenic which must be collected to give an absorbance of 0.0044 using this technique. For minimum absorbance of 0.100, a practical value for good precision and calibration linearity, the following proportion gives the amount of arsenic that must be collected:

$$\frac{Amount}{0.100} = \frac{0.02}{0.0044}\ \mu\text{g}$$

or $Amount = \frac{0.02}{0.044} * 0.100$ **= 0.45 μg**

Hence, 0.45 μg of arsenic must be collected to give an absorbance of 0.100 using the vapor generation technique. NIOSH recommends that the sampling and analytical method be sensitive enough to measure an airborne contaminant concentration of one-tenth the PEL, which is usually listed in units of milligrams per cubic meter of air. At this recommended minimum sensitivity, the concentration level for arsenic (PEL = 0.010 mg/m3) becomes 1 μg/m3. Since one cubic meter of air contains 1000 liters, this value become 0.001 μg/L when the units are converted. Another simple proportion then gives the minimum sample volume V, as indicated:

0.45 μg/V = 0.001 μg/L or V = **450 Liters**

The formula below summarizes these calculations:

$$V = \frac{cv}{0.0044\,(PEL)} \qquad (3)$$

where

V = minimum sample volume in liters required to obtain an absorbance of 0.100 at a contaminant concentration equal to one tenth the PEL
c = characteristic concentration in micrograms per millimeter
v = dilution volume for filter preparation in milliliters
PEL = Permissible Exposure Limit* in milligrams per cubic meter

A final inversion of the constant gives the following working formula, which can be utilized to quickly determine the nominal minimum sample volume:

$$V = \frac{230cv}{PEL} \qquad (4)$$

In our arsenic example,

$$V = \frac{230 * 0.0002\ \mu g\ /\ mL * 100\ mL}{0.010\ mg\ /\ m^3} \quad \mathbf{= 460\ L}$$

This nominal minimum sample volume should be collected to assure an absorbance of 0.100 using the vapor generation technique for analysis of air contaminated with one-tenth the OSHA PEL level of arsenic.

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* TLV (Threshold Limit Value) or Action Level value may also be substituted for PEL.

Minimum Sampling Time

How long to operate an air pump to sample some nominal volume of contaminated air is determined after pump calibration. Since pump flow rates are usually indicated in liters per minute, division of the nominal minimum air volume calculated above (in formula 4) by the calibrated pump flow rate gives the time as indicated by the following simple formula:

$$t = \frac{V}{r} \qquad (5)$$

where

t = sampling period in minutes
V = nominal volume of air to be sampled in liters
r = calibrated pump flow rate in liters per minute

Using a typical air pump flow rate of 2 L/min for our arsenic example,

$$t = \frac{460\ L}{2\ L/\min} = \mathbf{230\ min}$$

The minimum sample volume collected in some minimum sampling time (calculated above in formulas 4 and 5) represents the minimum amount of air which must be sampled to obtain an absorbance of 0.100 for a contaminant concentration equal to one tenth the PEL. This is a guide that may require adjustment if significantly larger or smaller contaminant concentrations are encountered.

Optimum Sample Volume

Selection of the optimum volume of air to sample depends upon various regulatory, operational, and analytical considerations such as:

- Regulatory constraints – Do any apply?
- Monitoring information – What is required?
- Frequency and duration of contamination – What exists in the workplace?
- Suspected contaminant concentration – What is it?
- Minimum volume – What will permit the best analysis?
- Maximum volume – What may limit the accuracy?

For example, the sample volume chosen may depend upon whether OSHA has mandated that full-shift samples be collected, whether CEILING values must be established, or whether the worker breathes contaminated air only occasionally and for short durations. In addition, if the suspected contaminant concentration is very low, the minimum volume may have to be increased. Or perhaps a high contaminant concentration exists and a maximum volume limit must be applied to prevent overloading of the filter. This listing is, of course, not all inclusive. Analysts and industrial hygienists must fully evaluate their particular application to determine the optimum sample volume necessary to obtain a representative sample.

Preparation of Filters for AA Analysis

MCE air filters are prepared for an AA analysis by dry ash, wet ash (or acid digestion), and extraction techniques. Ashing procedures involve decomposition of the filter and organic particulates. Extraction methods involve removal of the substance of interest from the filter. Since the subsequent AA analysis is best performed on a homogeneous solution of low viscosity and low acidity, these techniques generally include a sample dilution step.

Dry ashing usually involves placement of the filter sample in a crucible and heating it in a muffle furnace. The temperature is selected low enough to avoid loss of highly volatile analyte forms and high enough to ensure complete combustion of the filter and any organic particulates. Ashing at 500–550 °C for 4–16 hours is generally suitable. Although numerous procedural variations for dry ashing exist, some elements in some matrixes (for example, lead in the presence of chlorides) often cannot be subjected to dry ashing due to their high volatility.

Another dry ashing technique is low temperature oxygen plasma ashing. Although use of a lower temperature in a plasma ashing device prevents analyte loss due to volatility, the ashing time required may be up to 24 hours per sample.

Wet-ashing procedures are extensively used and recommended by NIOSH for IH air filter analyses by AA. Depending on the element analyzed and the AA technique utilized (flame, carbon rod, or vapor generation), various acid concentrations and mixtures may be utilized. In general, heating an MCE filter in a few milliliters of concentrated nitric acid completely decomposes the filter and dissolves particulate matter. Perchloric acid may also be required to oxidize certain organic substances present in the particulate matrix. A typical acid mixture is 5 mL conc. HNO_3 with 0.5 mL 60% $HCLO_4$, a 10:1 ratio of nitric to perchloric. Addition of this acid may cause volatility losses, especially for some samples analyzed with the carbon rod. Furthermore, due to the high reactivity of perchloric acid, its use is not recommended unless absolutely necessary. However, it can be used to decompose otherwise resistant organic substances in the particulate sample, provided that proper precautions are strictly observed.

Extraction of MCE filters is recommended by NIOSH when highly volatile forms of the analyte might otherwise be lost. Selenium, for example, is typically extracted with 0.1 percent nitric acid.

The selection of the best filter preparation scheme for an AA analysis depends upon the element to be analyzed, the nature of the particulate matter collected on the filter, and the methods available to the analyst. Consequently, although the NIOSH recommended procedures are a good starting point, IH analysts may have to make adaptations or develop their own filter preparation methods.

Blank Corrections

MCE filters, like analytical reagents, may contain significant amounts of the analyte of interest. Consequently, to avoid errors due to contributions by the filters themselves, a filter blank must be treated and analyzed in the same way as the sample filters are. It should not, of course, be used to actually sample any air. The amount of analyte determined in the filter blank must be subtracted from that found in the samples to obtain the correct air contaminant concentrations. In the NIOSH general AA procedure for metals (NMAM, Vol. 5), analysis of one filter blank is recommended for every ten sample filters.

Recovery

Biases in the analytical method can cause errors in exposure calculations. Determination of a recovery factor, however, can accommodate such errors. Typically, a known amount of the analyte (preferably nearly equivalent to that expected in the samples) is first placed onto duplicate MCE filters. These "spiked" filters along with a blank are then subjected to the same analytical procedure. After blank correction the recovery factor equals the weight spiked onto the filter divided by the weight obtained in the analysis.

$$\text{Recovery Factor, } F = \frac{Weight\ Spiked}{Weight\ Found} \qquad (6)$$

Multiplying the experimental IH sample weights by this recovery factor equals the corrected sample weight.

Corrected Sample Weight = F x Sample Weight Found

Conclusion and Summary

Unlike most other analytical techniques, the sampling procedure for an AA analysis of IH particulate samples involves two major technical fields, specifically, chemistry and industrial hygiene. Consequently, the typical general procedure for particulate sampling and AA analysis listed below often, requires the efforts of both a chemist and an industrial hygienist to efficiently and completely evaluate a worker's exposure to an airborne chemical contaminant.

List 1. Typical procedure for AA analysis of particulates on personal IH sample.

1. Find out the regulatory agency compliance requirements.
2. Estimate the expected contaminant concentration in the work space and time to decide whom, where, how long, how often, and in what manner to sample for compliance.
3. Check the applicable NIOSH analytical procedure and modify as necessary.
4. Calculate the nominal minimum air sample volume required to obtain an absorbance of 0.100 at one tenth the exposure limit. (Formula 4)
5. Set up and calibrate the sampling train. Note the flow rate*.
6. Calculate the minimum sampling period. (Formula 5)
7. Replace the calibration cassette with a sampling cassette.
8. Attach the sampling train to the worker. Clip the cassette face downward onto the worker's collar. Remove the inlet plug from the cassette.
9. Sample for some time period greater than or equal to the calculated minimum sampling time.
10. At the end of the sampling period, replace the end plug on the cassette and remove the sampling train from the worker.
11. Deliver the sampling cassette to the analytical laboratory.
12. Remove the MCE filter from the cassette.
13. Prepare the filter as required for the given analyte and particulate matrix.
14. Quantitatively dilute to some practical analysis volume.
15. Analyze by AA using the manufacturer's recommended operational parameters.
16. Determine the concentration of the diluted sample. (Calibration curve or direct instrumental readout. Correct for filter blank.)
17. Calculate the weight of analyte collected on the filter. (Dilution volume times the concentration determined in Step 16.)
18. Calculate the volume of air sampled. (Formula 1)
19. Calculate the concentration of the airborne contaminant sampled. (Weight of analyte calculated in Step 17 divided by volume of air calculated in Step 18.)
20. Record results as required for compliance.

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* Temperature and pressure corrections may also be necessary.

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Printed in the USA
November 1, 2010
AA003

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