Field-portable methods for monitoring occupational exposures to metals

By Kevin Ashley

INTRODUCTION

Millions of workers in the United States are exposed to inorganic toxic substances in myriad occupations. depending on the work practices, processes, techniques, and locations, workers may be exposed to airborne concentrations of a wide variety of metals and metalloids that may have toxic effects. Laborers in construction and mining are exposed to high concentrations of airborne heavy metals, and workers in some industries suffer exposures from toxic elements such as beryllium and hexavalent chromium on surfaces as well. In the U.S. alone, occupational lead exposures continue to result in high blood lead levels in hundreds of thousands of workers. Exposures to aerosols and vapors containing inorganic toxic agents can lead to numerous deleterious health effects, such as lung disease and damage to other organs, anemia, asthma, cancer, and neurological effects, to cite a few examples.

In 1970, the Occupational Safety and Health Act (Public Law 91-596) gave the National Institute for Occupational Safety and Health (NIOSH) responsibility for the development and evaluation of sampling and analytical methods for workplace exposure monitoring. Occupational exposure monitoring to toxic substances is conducted by public health professionals in order to determine whether exposures are in excess of pertinent occupational exposure limits (OELs), e.g., NIOSH Recommended Exposure Limits (RELs). Presently, the most commonly used method for assessment of worker exposures entails collection of air samples, which is followed by subsequent laboratory analysis. Generally speaking, metallic aerosols are collected onto filters which are subsequently analyzed in order to obtain an estimate of exposure. For aerosol collection, there has been recent interest towards the use of inhalable samplers, rather than ‘total’ aerosol samplers. Sampling of smaller size fractions, e.g., respirable or thoracic, may also be pertinent for exposure assessment involving metallic aerosols. Apart from air samples, in recent years there has been increased interest in monitoring of surface dust, since occupational exposures to toxic materials can sometimes occur via worker contact with contaminated surfaces. New work activities and processes have also resulted in a desire for novel industrial hygiene sampling and analysis techniques. All of these scenarios present new analytical challenges that need to be addressed.
To this end, much of the research effort in our laboratory has been directed towards the development, evaluation and validation of user-friendly procedures that can be employed for on-site monitoring of toxic metals in occupational environments. Construction and mining industries have been the primary targets of application for field-portable monitoring methods, but such procedures can be taken to other workplace environments as well, notably manufacturing. On-site methods for the determination of lead\(^{16,17}\) and hexavalent chromium\(^{18,19}\) in filter samples collected from workplace air have been used successfully in field studies. In addition to air filter samples, portable anodic stripping voltammetry (ASV) has also been shown to perform well for measuring lead in surface dust samples collected using wipes.\(^{20}\) Portable X-ray fluorescence (XRF) can provide on-filter quantitative measurement of a number of heavy metals in samples collected from workplace atmospheres.\(^{21}\) In other work, a molecular fluorescence method for the determination of trace beryllium in workplace air and wipe samples has been developed and validated.\(^{22}\) In several instances, field methods have been shown to meet NIOSH criteria for method accuracy.\(^{23}\)

The aim of this paper is to provide an overview of the available field-portable methods for metals that have been published as NIOSH methods and/or as ASTM International (formerly American Society for Testing and Materials) voluntary consensus standards. Depending on the specific application, definitive (quantitative), semi-quantitative and screening methods are all useful in the industrial hygiene field. Portable methods offering desired performance characteristics are available for some metals, notably lead, beryllium and chromium. Field screening test method performance has been treated in a general fashion using a rigorous statistical protocol,\(^{24}\) with applications having been demonstrated for examples entailing lead monitoring in the workplace.\(^{25}\) Using a statistical formalism to treat collected data, performance criteria and characteristics of field-portable methods can be estimated for qualitative, semi-quantitative, and quantitative measurement procedures. The application is general for any analyte, and allows for results from screening tests to be used in making defensible decisions concerning potential human exposures to toxic substances. This research provides a basis for investigations on the evaluation of field screening methods for toxic inorganic species of interest in occupational safety and health.

**NIOSH METHODS**

Field-portable analytical methods for metals that have been approved and published in the NIOSH Manual of Analytical Methods include examples of qualitative, semi-quantitative and quantitative procedures. Qualitative screening methods have been described by NIOSH for detecting lead in air filters, as well as for the detection of lead or hexavalent chromium in wipe samples. A semi-quantitative NIOSH method for estimating lead loadings in air filter samples, based on the use of portable XRF, has also been promulgated. Quantitative measurement procedures for metals that have been approved as NIOSH methods include: (a) lead determination in air samples by portable ASV; (b) determination of hexavalent chromium in air by portable spectrophotometry; and (c) on-site determination of beryllium in air filters or wipe samples by a molecular fluorescence technique. Salient details regarding these methodologies are provided in the following paragraphs.

A screening technique for testing for the presence of lead in air filter samples, NIOSH Method 7700,\(^{26}\) entails the use of a colorimetric chemical spot-test kit applied to the particulate matter collected on the filters. A characteristic color change on the filter (i.e., from yellow/orange to pink/red hues) indicates the presence of lead in the collected aerosol. To evaluate the method, a commercial rhodizinate-based spot test kit was evaluated for its potential use in the detection of lead in airborne particulate matter.\(^{27}\) Battery-powered personal sampling pumps were used to collect over 370 air samples on cellulose ester membrane filters at various worksites where lead was a suspected air contaminant. Each filter sample was tested with an individual chemical spot test, and the samples (test kit materials included) were then analyzed using reference measurement of lead by graphite furnace atomic absorption spectrometry (GFAAS) as described by NIOSH Method 7105.\(^{28}\) The experimental data were statistically modeled in order to estimate the performance parameters of the spot test kit. A positive reading was found at 95% confidence for lead mass values above about 10 \(\mu g\) per filter, while 95% confidence of a negative reading was found for lead masses below \(\leq 0.6 \mu g\) per filter.\(^{29}\) Given these performance measures, in the field the spot test screening technique can be used to estimate, using short- or medium-term sampling, whether lead exposures will be expected to exceed applicable OELs, e.g., the Occupational Safety and Health Administration (OSHA) Personal Exposure Limits (PELs) for lead, \(Tl^{+}, Ag^{+}, Cd^{2+}, Ba^{2+},\) and \(Sn^{2+}\) also form colored compounds with rhodizinate ion, but with less sensitivity than that of \(Pb^{2+}\), and only the lead–rhodizinate complex gives the characteristic pink or red color.\(^{30}\)

A similar colorimetric screening method for the presence of lead in wipe samples has been described in a NIOSH procedure.\(^{31}\) The method was designed as a handwipe method for detecting lead collected from human skin,\(^{32}\) but it is also applicable to wipe samples obtained from various non-dermal surfaces including floors, walls, equipment, furniture, etc. The method has been evaluated preliminarily using commercial wipes spiked with certified reference materials (CRMs), and has been found to give a positive response for at least 10 \(\mu g\) of lead per wipe. The method has also been subjected to limited field testing, and shows a positive response for at least a few tens of micrograms of lead per wipe. Extremely heavy soiling on the wipe could interfere with visualization of the red color change due to darkening of the wipe, but the pink or red hues should still be visible around the area of the heaviest soiling, provided lead is present. Difficult matrices (e.g., dust wipes
containing paint chips) may require leaching in dilute nitric acid before spot testing. In addition to the metallic interferences mentioned above for air filter samples screened using rhodizone-based test kits, interferences from the wipe medium, e.g., surfactants, are also possible.

Hexavalent chromium, Cr(VI), can be detected colorimetrically at trace levels using diphenylcarbazide, and this chemistry has been applied to the detection of Cr(VI) in wipe samples. The method reportedly can detect masses as low as a microgram of Cr(VI) per sample, but unfortunately no evaluation data are available. In any case, a qualitative screening procedure could be useful to detect traces of Cr(VI) in surface dust collected using wipes. Follow-up analysis with more definitive methods is recommended.

Portable XRF measurement of lead in aerosols collected onto air filters has been described in a NIOSH method. This methodology was validated on field samples by collecting lead particulate samples from bridge lead abatement projects. Airborne concentrations of lead within the containment area of a sand blasting bridge lead abatement project ranged from 1 to 10 mg/m³. Area and personal samples were collected for periods of time ranging from 15 s to 2 hours. This sampling protocol yielded 65 filter samples with lead loadings ranging between 0.1 and 1,500 µg of lead per sample. The filter samples obtained were first analyzed using a non-destructive, field-portable XRF method, and the samples were subsequently subjected to reference analysis by the laboratory-based NIOSH Method 7105.28 The portable XRF method was statistically evaluated in accordance with NIOSH guidelines.23 The overall precision of the portable XRF method was calculated at 0.054 (95% confidence interval (CI) = 0.035–0.075), and the bias was 0.069 (95% CI = 0.006–0.152). The portable XRF method accuracy was determined to be ±16%; however, at the upper 90% CI, the accuracy is ±27%. Since the confidence interval exceeds ±25%, meeting the NIOSH accuracy criterion23 is inconclusive; hence, this measurement technique may be regarded as “semi-quantitative”. However, it is noted that the samples used to evaluate the portable XRF method were field samples; laboratory-prepared aerosol samples give better precision.21 Additionally, it should be pointed out that the portable XRF method is non-destructive; if required, samples analyzed on-site in the field can subsequently be transported and analyzed in a fixed-site laboratory using a method with greater accuracy. Portable XRF may also be extendable to the determination of lead on surfaces after collection using wipe media.23

Quantitative on-site analysis of air filter samples for the determination of lead by field-based ultrasonic extraction with ASV measurement has been published as a NIOSH method.36 This method was evaluated with lead aerosol samples generated in the laboratory (∼40 to ∼80 µg Pb per filter), and with air particulate samples collected from workplaces where abrasive blasting of leaded paint on highway bridges was being conducted.38 For the latter, lead masses covered the range from below the detection limit of 0.09 µg Pb per filter to loadings in excess of 1,500 µg Pb per filter. The method also has been evaluated with performance evaluation materials and by interlaboratory testing.39 Lead recoveries from CRMs were found to be quantitative (>90%) and equivalent to recoveries obtained using confirmatory analytical methods (e.g., NIOSH 710528). Thallium is a known interferant, but its presence is unlikely in the vast majority of occupational air samples. Extremely high concentrations of copper may cause a positive bias. Surfactants can poison electrode surfaces, so if the presence of surfactants is suspected, such interferences must be eliminated during sample preparation.

A quantitative method describing the trace determination of beryllium in air samples by field-based extraction and fluorescence measurement has been published in the most recent edition of the NIOSH Manual of Analytical Methods.40 The method entails extraction of beryllium in air filter samples for 30 min using dilute (1%, aqueous) ammonium bifluoride, with subsequent fluorescent measurement after reaction of dissolved beryllium dication with the high-quantum yield fluorophore, hydroxybenzoquinoline sulfonate.22 Experiments were conducted using several commercial portable fluorescence devices. The method was evaluated using beryllium oxide spiked onto mixed-cellulose ester (MCE) filters at various levels (0, 0.02, 0.1, 0.2, 0.3, 0.4, 1.5, 3.0, and 6.0 µg; five samples at each level). Long-term stability of samples was verified from spikes (number [n] = 30) of 0.1 µg Be on MCE filters. Samples were analyzed at day one (n = 12) and then 1 week (n = 6), 10 days (n = 3), 2 weeks (n = 3), 3 weeks (n = 3), and 1 month (n = 3) after spiking. No diminution of fluorescence signal was observed from samples prepared and analyzed after having been stored for up to 30 days. Interference tests were carried out using solutions of 0 nmol/L, 100 nmol/L, and 1.0 µmol/L Be in the presence of 0.4 mmol/L of Al, Ca, Co, Cu, Fe, Ti, Li, Ni, Pb, Sn, U, V, W, or Zn (separate experiments were carried out for each potential interferant). Minor interference from iron can result if iron concentrations are high (e.g., ∼100× the beryllium concentration). Samples high in iron demonstrate a yellow or gold coloration. This interference can be minimized by allowing the solution to sit for 4 hours or more, during which time the solution clears, and then filtering the sample extract before use. Interlaboratory evaluations of the method were also performed on both soluble and refractory beryllium compounds.22,41 When high-temperature (∼90°C) extraction is employed, the method is effective for quantitative dissolution and determination of high-fired (calcined) beryllium oxide in aerosol samples. Ultra-trace determination of beryllium in air samples has been achieved, with attainable method detection limits of less than a nanogram of beryllium per sample.41 It is pertinent to note that the method detection limit of the portable fluorescence method for beryllium is comparable to that of inductively coupled plasma mass spectrometry (ICP-MS).42 A companion NIOSH method for determining beryllium in surface wipe
### Table 1. NIOSH field-portable methods for metals measurement in samples collected in occupational settings

<table>
<thead>
<tr>
<th>Method number</th>
<th>Sample medium</th>
<th>Element/species</th>
<th>Sample preparation</th>
<th>Detection method</th>
<th>Estimated MDL&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>7700</td>
<td>Air filters</td>
<td>Pb</td>
<td>Extraction (weak acid)</td>
<td>Colorimetry (chemical spot test)</td>
<td>&lt;10 µg/sample</td>
</tr>
<tr>
<td>7701</td>
<td>Air filters</td>
<td>Pb</td>
<td>Ultrasonic extraction (dilute HNO&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>Anodic stripping voltammetry</td>
<td>0.09 µg/sample</td>
</tr>
<tr>
<td>7702</td>
<td>Air filters</td>
<td>Pb</td>
<td>None</td>
<td>X-ray fluorescence</td>
<td>6 µg/sample</td>
</tr>
<tr>
<td>7703</td>
<td>Air filters</td>
<td>Cr(VI)</td>
<td>Ultrasonic extraction (sulfate or carbonate buffer)&lt;sup&gt;d&lt;/sup&gt;; SPE&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Spectrophotometry</td>
<td>0.08 µg/sample</td>
</tr>
<tr>
<td>7704</td>
<td>Air filters</td>
<td>Be</td>
<td>Extraction (dilute NH&lt;sub&gt;4&lt;/sub&gt;HF&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>Fluorescence</td>
<td>0.0008 µg/sample</td>
</tr>
<tr>
<td>9101</td>
<td>Wipes</td>
<td>Cr(VI)</td>
<td>Extraction (dilute H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;; pH adjustment (carbonate buffer))</td>
<td>Colorimetry (chemical spot test)</td>
<td>1 µg/sample</td>
</tr>
<tr>
<td>9105</td>
<td>Wipes</td>
<td>Pb</td>
<td>Extraction (weak acid)</td>
<td>Colorimetry (chemical spot test)</td>
<td>~10 µg/sample</td>
</tr>
<tr>
<td>9110</td>
<td>Wipes</td>
<td>Be</td>
<td>Extraction (dilute NH&lt;sub&gt;4&lt;/sub&gt;HF&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>Fluorescence</td>
<td>0.0008 µg/sample</td>
</tr>
</tbody>
</table>

<sup>a</sup> Method detection limit.<sup>b</sup> With minor modification, method is also applicable to wipe samples.<sup>c</sup> With modification, method may also be applicable to wipe samples.<sup>d</sup> For soluble or insoluble Cr(VI) compounds, respectively; addition of phosphoric acid is recommended for samples high in iron.<sup>e</sup> Solid-phase extraction; for many sample matrices, this step can be omitted.

Method evaluation and validation on cellulose fiber samples was carried out in a similar fashion as described above for air filter samples. Trace and ultra-trace quantitative determination of beryllium in wipe samples has been demonstrated, along with excellent intra- and inter-laboratory reproducibility. A modification of the procedure, in which longer-term extraction (4 hours) is carried out in a slightly higher concentration (3%) of aqueous ammonium bifluoride, enables quantitative extraction of larger particle sizes (up to >200 microns aerodynamic diameter) of high-fired beryllium oxide. The method yielded acceptable recoveries from refractory BeO in several different sampling media tested.

A field-portable spectrophotometric NIOSH method for determining Cr(VI) in air filter samples entails field-based ultrasonic extraction in basic buffer, followed by measurement of the chromium–diphenylcarbazide adduct. Strong anion-exchange solid-phase extraction (SAE-SPE) enables isolation of Cr(VI) from other metallic interferants such as trivalent iron, manganese and mercury. This method was evaluated in the laboratory with spiked filters and with a CRM containing a certified loading of Cr(VI). (This European CRM, consisting of Cr(VI) and Cr(total) in welding dust loaded on a glass fiber filter, is no longer available.) The NIOSH portable method for Cr(VI) has also been evaluated in the field, where samples collected during aircraft maintenance and painting operations were analyzed on-site. Filters used for sample collection can be pretreated with base to minimize Cr(VI) reduction during sampling in high-iron or acidic environments.

**ASTM METHODS**

Voluntary consensus standards such as those published by ASTM International are considered by many to be the most technically sound and most credible documents for use in their particular fields of application. This was recognized by the U.S. Congress through passage of the National Technology Transfer and Advancement Act of 1995 (Public Law104-113), which directs federal agencies to: (a) rely on consensus standards in their guidelines and activities, and (b) participate in the consensus standards development process. Experts from relevant federal agencies have contributed significantly to the development of numerous ASTM standards that apply to the field of industrial hygiene chemistry. Within ASTM International Committee D22 on Workplace Air Quality, Subcommittee D22.04 on Workplace Air Quality produces standards that describe methods to collect and measure chemical hazards in the workplace. This committee has been active for decades, and its members have developed many needed standards consisting of test methods, practices, and guides. These consensus standards are meant for use by industrial hygienists, chemists, engineers, health physicists, toxicologists, epidemiologists, and myriad other professionals. Experts from private industry, government, and academia have all contributed extensively to the development of standards for workplace contaminant monitoring. One of the voluntary consensus standards produced by ASTM International Subcommittee D22.04 describes field-portable procedures for trace beryllium monitoring. Also, ASTM International Subcommittee E06.23 on Mitigation of Lead Hazards has published several standards pertaining to on-site measurement of lead in occupational environments.
and analysis of beryllium and lead in occupational environments are given below.

ASTM D7202 describes a test method that is intended for use in the determination of beryllium by sampling workplace air or surface dust. The method assumes that air and surface samples are collected using appropriate and applicable ASTM International standard practices for sampling of workplace air and surface dust. These samples are typically collected using air filter sampling, vacuum sampling, or wiping techniques. The method includes a procedure for on-site extraction (dissolution) of beryllium in weakly acidic medium (pH of 1% aqueous ammonium bifluoride is 4.8), followed by field analysis of aliquots of the extract solution using a beryllium-specific fluorescent dye, hydroxybenzoquinoline sulfonate. The procedure is targeted for on-site use in the field for occupational and environmental hygiene monitoring purposes, and can be used to determine as low as a few nanograms of beryllium in collected samples. This voluntary consensus standard method was developed based on the aforementioned NIOSH procedures for on-site determination of beryllium in the workplace.

Lead contamination in paint, dust, soil and air represents a potential health hazard to people, and field-portable analytical methods for the determination of this toxic metal in environmental samples are desired for the on-site assessment of lead hazards. On-site determination of lead in occupational hygiene samples obtained using consensus standard sampling techniques is described in ASTM procedures for field-based ultrasonic extraction and electroanalysis (e.g., ASV), respectively. These ASTM standards were developed based on the NIOSH method described earlier. Compared to traditional digestion methods that employ hot plate or microwave digestion with concentrated acids, ultrasonic extraction using dilute nitric acid is a simple, yet effective, method for extracting lead from air filter and wipe samples. Hence, ultrasonic extraction may be used in lieu of the more rigorous strong acid/high-temperature digestion methods, provided that the overall method performance is demonstrated using acceptance criteria as delineated in ASTM Guide E1775. In contrast with hot plate and microwave digestion techniques, the equipment required for ultrasonic extraction is field-portable, which allows for on-site sample analysis.

Field-portable techniques (such as ASV) for the determination of lead in environmental and occupational hygiene samples, notably air filters and wipe samples, may allow for rapid assessments of lead hazards and corresponding cost reductions compared to traditional fixed-site laboratory-based analyses. Prior to analysis in accordance with ASTM standard protocols, the use of standardized sampling techniques for lead in air and on surfaces is highly recommended. Moreover, for leaded dust wipe sampling, it is urged to use a standardized wipe material. Standardization of sampling materials, sample collection procedures, sample preparation protocols, and analytical methods is meant to optimize overall analytical performance and interlaboratory comparability. Using these ASTM standard methods, practices, guides and specifications, on-site measurement of lead content in workplace samples may be used for compliance with applicable federal, state, and local regulations and guidelines, providing accepted performance criteria are demonstrated to be met.

Table 2 provides an overview of the ASTM standards relating to the field-portable methods for metals described in this section.

**CONCLUDING REMARKS**

Traditionally, workplace samples for subsequent metals determination have been sent away to fixed-site laboratories for analysis. In some cases, the analytical results can take many weeks to be reported. Such delays can compromise worker health if exposures are excessive. The use of field-portable methods and instrumentation for on-site metals monitoring is meant to alleviate such problems that may be
brought on by delayed analytical results. Methods relying on field-portable instruments and tests allow for screening and/or analysis of occupational hygiene samples on location with same-day speed. \(^6\) While most of the methods described in this paper do not rely on direct-reading monitoring techniques, they are nonetheless invaluable for obtaining rapid analysis results. Additionally, samples that are analyzed non-destructively in the field can be sent for confirmatory analysis if exposures appear to approach or exceed applicable OELs. This can reduce the number of samples that are conveyed to fixed-site laboratories and makes the overall exposure assessment process more cost-effective. Use of field-portable methods can also facilitate the proper selection and evaluation of exposure controls to reduce the potential for adverse health effects among workers. The NIOSH and ASTM International methods and standards highlighted in this article represent accepted government and consensus standard procedures for on-site monitoring of metals, notably lead, beryllium and hexavalent chromium. \(^8\) While there is redundancy between some of the NIOSH and ASTM field-portable analytical methods discussed here, the availability of voluntary consensus standards is often desired by potential users. Also, reliance on consensus standards may be required by accreditation and certification bodies.

ACKNOWLEDGMENTS

Appreciation is extended to Leroy Dobson of the Wisconsin Occupational Health Laboratory, as well as Yvonne Gagnon, Bob Streicher and Dave Utterback of NIOSH, for reviewing the draft manuscript.

REFERENCES


