

Field-portable methods for monitoring occupational exposures to metals[☆]

Millions of workers are employed in manufacturing, mining, construction, and other industries where significant amounts of airborne metals and metal compounds are generated. Depending on the work practices, processes, techniques, and locations, exposures to airborne and surface sources of a variety of metals can cause occupational illness. These exposures can lead to a plethora of adverse health effects such as lung disease, anemia, cancer, asthma, dermal sensitization, dermatitis and neurological damage. The ability to monitor worker exposures to metals on-site in the field has been a goal of the National Institute for Occupational Safety and Health (NIOSH) since the early 1990s. In the last 15 years or so, several field-portable procedures for metals have been developed, evaluated and published as NIOSH methods. These methods, published in the *NIOSH Manual of Analytical Methods*, describe field screening tests and on-site analysis for lead, hexavalent chromium and beryllium. Some of these methods have also been published in the form of ASTM International voluntary consensus standards. This paper gives an overview of NIOSH research and development efforts on field screening and portable analytical methods for metals in the workplace. The goal of such efforts has been to provide screening and analytical tools that can be used on-site in the field to aid in the prevention of excessive exposures to toxic metals in the workplace.

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INTRODUCTION

Millions of workers in the United States are exposed to inorganic toxic

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substances in myriad occupations.¹ 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,² and workers in some industries suffer exposures from toxic elements such as beryllium³ and hexavalent chromium⁴ 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.⁵ 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.^{6,7}

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).⁸ 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 filters⁹ which are subsequently analyzed in order to obtain an estimate of exposure.¹⁰ For aerosol collection, there has been recent interest towards the use of inhalable samplers, rather than 'total' aerosol samplers.^{11,12} Sampling of smaller size fractions, e.g., respirable or thoracic, may also be pertinent for exposure assessment involving metallic aerosols.¹³ Apart from air samples, in recent years there has been increased interest in monitoring of surface dust,¹⁴ 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.¹⁵ 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 rhodizonate-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 mem-

brane 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 µg Pb per filter, while 95% confidence of a negative reading was found for lead masses below ≈0.6 µg Pb per filter.²⁷ 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 rhodizonate ion, but with less sensitivity than that of Pb^{2+} , and only the lead-rhodizonate complex gives the characteristic pink or red color.²⁹

A similar colorimetric screening method for the presence of lead in wipe samples has been described in a NIOSH procedure.³⁰ The method was designed as a handwipe method for detecting lead collected from human skin,³¹ 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 µg 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

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