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Instrument Performance Criteria

Mary Lynn Woebkenberg Column Editor [a] & Kevin Ashley [a]

[a] National Institute for Occupational Safety and Health, Cincinnati, Ohio, 45226, USA

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Instrument Performance Criteria

On-Site Extraction and Anodic Stripping Voltammetric Determination of Lead

Mary Lynn Woebkenberg, Column Editor

Reported by Kevin Ashley

Introduction

The class of instruments covered in this article involves field-portable electroanalysis of lead, preceded by ultrasonic extraction (UE) of workplace air samples or environmental samples. The electroanalytical instruments are portable, battery-powered devices that employ anodic stripping voltammetry (ASV) to effect the determination of lead. UE of lead from workplace air samples and environmental matrices is accomplished by using a sonicator which may be employed on site in the field. ASV can be used to measure trace quantities of a number of metals in solution, and is especially useful for lead determination in environmental and industrial hygiene samples. Ultrasonic energy can be used for the extraction of a number of organic and inorganic species, and has been shown to perform very well for lead extraction. The UE/ASV technique forms the basis of a new National Institute for Occupational Safety and Health (NIOSH) method for lead in air for the field-based determination of lead in workplace air samples. The equipment can also be used for the determination of lead in environmental samples such as paint, dust, and soil.

Basic Operating Principles

Sample Collection

Airborne particulate lead is collected using the standard air sampling technique employing a cellulose ester membrane filter cassette connected in-line to a personal sampling pump.(1) Workplace air samples are generally collected closed-faced for the entire work period for 8-hour time-weighted average (TWA) exposure monitoring. However, short-term sampling may also be done in order to investigate exposures from specific work practices or activities.

Ultrasonic Extraction

Extraction of lead from airborne particulate material collected onto a cellulose ester membrane filter is accomplished with the aid of an acid solution and ultrasonic energy. The filter is immersed in a diluted nitric acid solution (10% v/v HNO_3/H_2O) within a centrifuge tube. The tube is then placed in an ultrasonic bath (Figure 1), and the contents are subjected to ultrasonic energy for a minimum of 30 minutes. Ultrasonic energy generates extremely high local temperatures and pressures, and also causes bubble formation (cavitation), at boundaries between solid and liquid phases.(2) This combination of temperature, pressure, and physical effects upon the solid matrix containing undissolved lead particles causes these particles to break up, with the concomitant acid-assisted dissolution of lead in its cationic form (Pb^{2+}). UE has been shown to be effective for the dissolution of lead from a number of environmental matrices, including paint, soil, dust, and airborne particulate samples.(3–6)

Anodic Stripping Voltammetry

ASV is an electroanalytical technique in which the concentration of analyte metal species (lead for our purposes here) dissolved in solution is determined in the following manner (Figure 2). The lead originally dissolved by UE (as described previously) is first deposited (preconcentrated) electrochemically. This is done by reducing the dissolved metal ion (Pb^{2+}) at an applied potential (voltage) E_D to immobilized discharged metal species (Pb^o) at a working electrode surface (ordinarily mercury):

$$Pb^{2+} \text{ (solution)} + 2e^- \rightarrow Pb^0 \text{ (Hg electrode)} \quad \text{(at potential E)}$$

This is accomplished by applying an electrode potential which is sufficiently negative (with respect to the reference electrode) to cause reduction (gain of electrons) of solubilized lead ions. The metal is deposited in the form of an amalgam (with mercury) at an applied potential that is negative of the standard redox potential of the metal/ion redox couple. (E_D must be negative of the standard potential E° for the Pb/Pb^{2+} redox couple in order to cause the above reduction.) After deposition for a given time period t_d, the preconcentrated lead species is then stripped from the working electrode surface by applying a positive potential sweep. This causes anodic oxidation (loss of electrons) of the amalgamated, discharged (Pb^o) lead species to dissolved ion (Pb^{2+}). This occurs at an applied potential E_{app} which is sufficiently positive to effect reoxidation of the lead originally deposited at E_D:

$$Pb^0 \text{ (Hg electrode)} \rightarrow Pb^{2+} \text{ (solution)} + 2e^- \quad \text{(at potential } E_{app}\text{)}$$

(E_{app} must be positive of the standard potential E° for the Pb/Pb^{2+} redox couple in order to cause the above oxidation.) During the stripping step, the current associated with this reoxidation is measured (Figure 3). The peak current i_p arising from the reoxidation of discharged, amalgamated lead species is proportional to the original concentration of dissolved lead ion over a wide range of concentrations.(3,4,7) ASV is extremely sensitive, and field-portable ASV can measure lead concentrations in the parts per billion range in solution.

Applications

UE/ASV determination of lead is a relatively new technique available for use by industrial hygienists and environmental health scientists. A new NIOSH method based on UE/ASV, Method No. 7701, has recently been evaluated and added to the *NIOSH Manual of Analytical Methods*. The UE/ASV method can be used for the determination of lead concentrations

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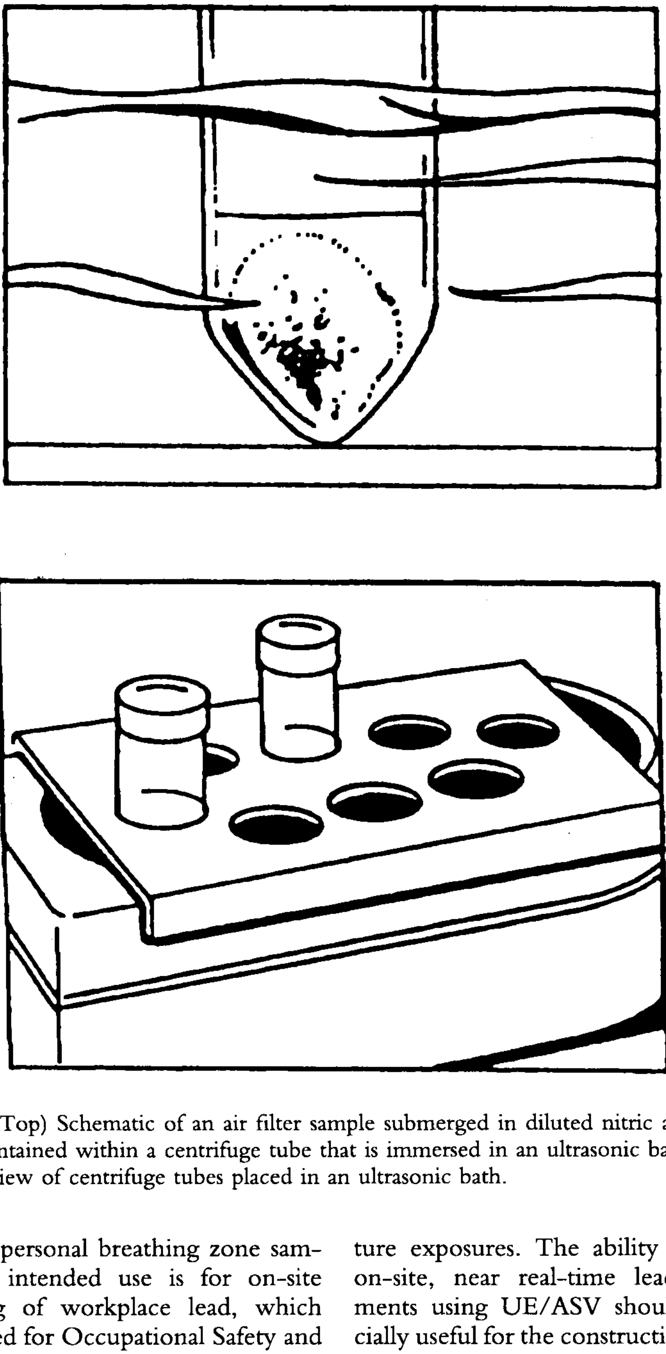

FIGURE 1. (Top) Schematic of an air filter sample submerged in diluted nitric acid solution, which is contained within a centrifuge tube that is immersed in an ultrasonic bath. (Bottom) Expanded view of centrifuge tubes placed in an ultrasonic bath.

in area or personal breathing zone samples. The intended use is for on-site monitoring of workplace lead, which may be used for Occupational Safety and Health Administration (OSHA) compliance purposes in construction (29 CFR 1926.62) as well as in general industry (29 CFR 1910.1025).

The ability to measure lead on site in the field precludes the need to send samples away for laboratory analysis. Hence, exposure assessments can be made much more quickly, since there is no need to wait for laboratory results before personal exposure data can be examined. Therefore, rapid decisions regarding personal protective equipment and/or engineering controls can be made to prevent future exposures. The ability to perform on-site, near real-time lead measurements using UE/ASV should be especially useful for the construction industry, where jobs are frequently short-term and worker turnover is often high. The capability for on-site exposure monitoring can greatly speed up industrial hygiene work and reduce costs associated with job down time and laboratory analysis. More important, this capability can reduce worker overexposures to lead, since exposure assessments using UE/ASV data can be done quickly in order to decide the necessary level of respiratory protection.

The performance of UE/ASV for two portable ASV instruments has been evaluated(3,4) (Table 1). UE was carried out using standard laboratory sonicators. No bias was identified for either portable ASV instrument. In both cases the performance meets NIOSH accuracy criteria for a sampling and analytical test method.(8) (The NIOSH accuracy criterion states that the measured value must be within ±25% of the true value at least 95% of the time. The accuracy is a function of the estimated precision and bias of the method.) For comparison with the entries in Table 1, the OSHA permissible exposure limit for an 8-hour TWA sample taken at about 2 L/min is approximately 50 μg/sample:

$$480 \text{ min} \times 2.0 \text{ L/min} = 960 \text{ L}$$

$$50\ \mu\text{g/m}^3 \times 0.960 \text{ m}^3$$

$$= 48\ \mu\text{g/sample}$$

The UE process requires 30 to 45 minutes, but this is a much shorter time period than that required for conventional extraction methods using hot plate or microwave strong acid digestion. Numerous samples can be sonicated at one time, the maximum number depending on the size of the bath. Commercial ultrasonic baths are not battery powered and therefore require an electric power source. If necessary (i.e., if no electric power source is available), a portable generator may be used in the field. The ASV analysis takes only a minute or two per sample, so the most time-consuming portion of the overall analysis (once samples are collected, of course) is sample preparation. The portable ASV device can be interfaced to a laptop computer for on-site downloading and treatment of field data.

Apart from workplace air sampling and analysis, the UE/ASV technique can also be applied to the analysis of lead in a variety of other environmental matrices. UE/ASV has become an acceptable method under the U.S. Environmental Protection Agency (EPA) National Lead Laboratory Accreditation Program (NLLAP).(9) Analytical methods that are deemed acceptable under NLLAP are evaluated for their acceptance in the Environmental Lead Proficiency Analytical Testing program.(10) Hence, the UE/ASV technique may be used to measure lead in paint, dust, and soil samples in the lead hazard control arena.(11) For example, UE/ASV analyses can be used to

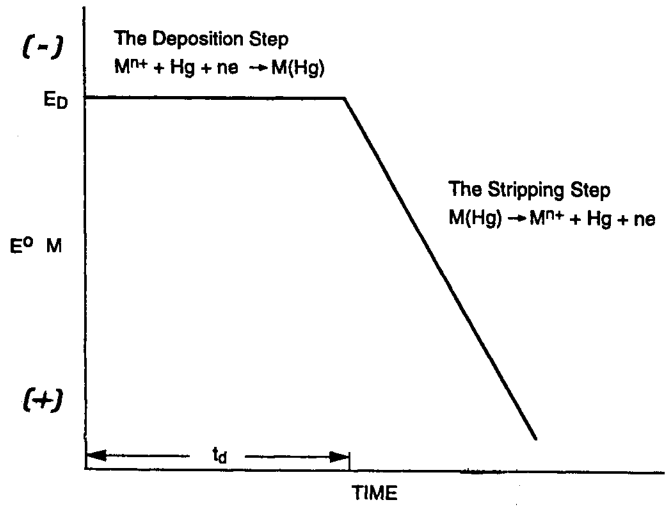

FIGURE 2. Potential time sequence used in ASV. E_D, deposition potential; E^o M, standard potential for the M/M^{n+} redox couple; M, metal analyte species; n, number of equivalents transferred during redox reaction; e, electrons; t_d, deposition time.

assure compliance with the requirements of Title X, the Residential Lead Hazard Control Act of 1992 (Public Law 102-550). Additionally, UE is an accepted EPA method for the dissolution of lead from air samples for ambient air monitoring purposes (40 CFR 50, Appendix G). ASV could be used for subsequent analysis of ultrasonically extracted ambient air samples.

Limitations

To date, the application of UE/ASV is limited to nonbiological environmental samples. Evaluation of the use of this methodology on biological samples such as blood, saliva, and other body fluids; foods; and plants is currently underway.

Interference from thallium is problematic, since the thallium stripping peak coincides with that of lead. However, thallium is expected to be present in very few environments where lead is an analyte of interest, so this interference should be a very rare occurrence. High concentrations of copper may interfere with ASV determination of lead by causing a positive bias. Hence, if high levels of copper are suspected, efforts must be taken to separate copper from lead during sample preparation. Also, surfactants and proteins can poison electrode surfaces, so if the presence of these agents is suspected, they must be eliminated during sample preparation.[12]

The training level required to carry out the UE/ASV method is reasonably high. Experience with quantitative chemical analysis is desirable. Training for UE/ASV analysis of lead in environmental samples is available from at least one instrument manufacturer.

Maintenance

The lifetime of ultrasonic baths is finite, and they must be tested periodically to ensure proper performance. Smaller baths of lesser power rating tend to last much less time than do larger, more powerful units. Fluid must be kept in the baths at all times during operation.

Electrodes used for ASV are fragile and rather expensive, but they are much more robust and less expensive than those used in the past for laboratory-based electroanalysis. ASV instruments employing renewable electrodes require more maintenance than those using disposable electrodes. This is because the working and reference electrodes must be maintained constantly in an electrolyte solution. Also, care must be taken to prevent the application of excess voltages. Electrical connections between analyte solutions and ASV instruments can become fouled rather easily (this is especially true for devices utilizing disposable electrodes), and require refurbishing when electrical connection is lost. Batteries must be replaced or recharged periodically.

Applicable Regulations

OSHA: 29 CFR 1910.1025, Lead, Occupational Safety and Health Standards (General Industry).
OSHA: 29 CFR 1926.62, Lead Expo-

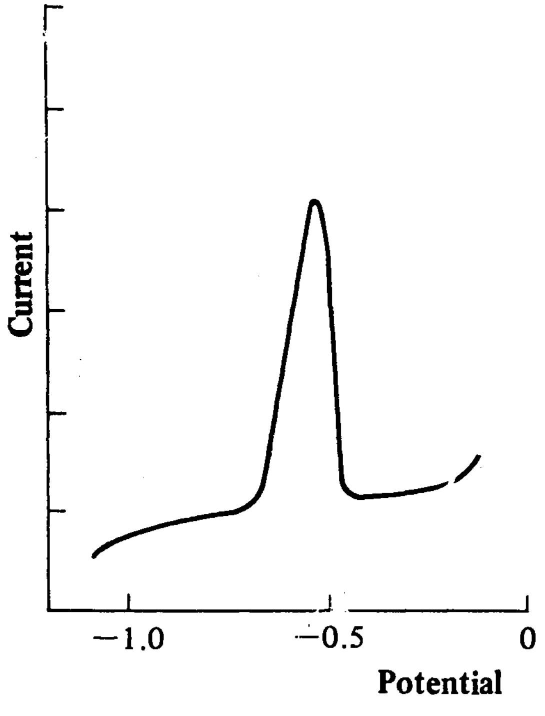

FIGURE 3. Representative anodic stripping voltammogram for lead. Current is in microamperes; potential is in volts versus Ag/AgCl reference electrode.

TABLE 1. Performance of Ultrasonic Extraction and Portable Anodic Stripping Voltammetry for Workplace Air Monitoring

Instrument	Detection Limit	Range	Accuracy
Chemtronix[A]	0.09μg/sample	0.31–1000μg/m^3	±19.3% (n = 51)
PaceScan[B]	2.5 μg/sample	25–1500μg/m^3	±17.2% (n = 74)

See References 3 and 4.
[A] Employs renewable electrodes.
[B] Employs disposable electrodes.

sure in Construction, Interim Final Rule.

U.S. EPA: 40 CFR 50—Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air (Appendix G).

Title X: Residential Lead-Based Paint Hazard Reduction Act; Public Law 102-550.

[Information on how to get copies of these regulations may be obtained by calling the Lead Hotline at (800) 424-LEAD.]

Pertinent Standards

ASTM PS 88, Provisional Standard Practice for the Determination of Lead in Paint, Settled Dust, Soil, and Air Particulate by Field-Portable Electroanalysis.

ASTM E1553, Standard Practice for Collection of Airborne Particulate Lead During Abatement and Construction Activities.

ASTM E1775, Standard Guide for Evaluating the Performance of On-Site Extraction and Field-Portable Analysis for Lead.

[Information on these and other ASTM standards may be obtained from the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428; (610) 832-9585.]

Instruments

Ultrasonic Baths

There are many manufacturers of ultrasonic bath devices. Ultrasonic baths of 50-W minimum power are recommended for field use. Costs of sonicators range from a few hundred dollars to thousands of dollars; those for field applications will be found on the lower end of the cost scale. The reader is referred to commercial catalogs for specific information on manufacturers of ultrasonic baths.

Portable ASV Devices

To date, only two commercially available portable ASV instruments are known to this author. There are many manufacturers of laboratory ASV instruments, but only information on portable ASV devices is given here. Both portable devices may be interfaced to a laptop or personal computer.

CHEMTRONIX PDV 2000 ANODIC STRIPPING VOLTAMMETER. Manufactured in Australia; distributed in North America by Metorex, 860 Town Center Drive, Langhorn, Pennsylvania 19047; (215) 741-4482. The Chemtronix instrument employs a rechargeable 24-V NiCd battery or an external electrical connection (110 to 220 V). It weighs 15 kg and has been on the market since 1986. Cost of the instrument is approximately $15,000. The device may be used for the analysis of other metals besides lead. Kits are provided for the analysis of a number of heavy metals. The glassy carbon working electrode can be used for thousands of analyses before replacement; replacement electrodes cost approximately $500. Built-in Ag/AgCl reference and Pt counter electrodes are provided; replacement reference electrodes cost approximately $150. The Chemtronix PDV 2000 requires a high training level.

PACESCAN 3000 SYSTEM. Manufactured in the United Kingdom; available in North America from Pace Environs, 207 Rutherglen Drive, Cary, North Carolina 27511 or 120 West Beaver Creek Road, Unit 16, Richmond Hill, Ontario L4B 1L2, Canada; (800) 361-5323. The PaceScan device uses 12 AA batteries and does not offer an external electrical connection. It weighs less than 1 kg and became commercially available in 1993. The cost of the instrument is approximately $4000, and it is dedicated to lead analysis. Electrodes are disposable (screen printed), cost about $5 each, and may be used for one analysis each. Each disposable electrode contains the working and reference (as well as counter) electrodes. Kits are available for lead analysis of various environmental matrices. The PaceScan 3000 requires a medium training level.

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Disclaimer

Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention.

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Note added in proof:

Since the time of this writing, the ownership of the PaceScan anodic stripping voltammetry (ASV) equipment has changed hands. Portable ASV instrumentation for lead determination, formerly sold by Pace Environs, Inc., is now available from Palintest USA, P.O. Box 18733, Erlanger, KY 41018; phone (800) 835-8629; fax (609) 341-2106; web site: http://www.palintestusa.com. Palintest USA is marketing the portable ASV lead instrument as the Palintest SA5000 Scanning Analyzer, which replaces both the PaceScan 2000 and 3000.

EDITORIAL NOTE: Kevin Ashley is a research chemist at the U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Cincinnati, Ohio 45226.