Short Communication

Ultrasonic Extraction and Field-Portable Anodic Stripping Voltammetry of Lead from Environmental Samples

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Abstract

Ultrasonic extraction of lead from environmental samples, followed by anodic stripping voltammetric (ASV) analysis using a field-portable ASV instrument, was evaluated. Representative lead-containing standard reference materials were subjected to ultrasonic agitation in dilute nitric acid, and the lead subsequently determined by ASV. Recoveries of lead were found to be statistically equivalent to those obtained previously by means of hotplate concentrated acid digestion and atomic spectrometric analysis. Laboratory-prepared air filter samples were also analyzed for lead content by using the ultrasonic extraction/portable ASV analytical protocol. For duplicate laboratory-prepared air filter samples, results from microwave digestion and atomic absorption analysis compared well with those from ultrasonic extraction and portable ASV analysis. The lower detection limit for the ultrasound/portable ASV method was found to be less than 1 ppb Pb in solution, or $< 0.1\ \mu g$ Pb/filter. The results suggest that the method may allow for the on-site determination of lead in environmental samples such as paint, dust, soil and workplace air.

Keywords: Anodic stripping voltammetry, Lead, Trace environmental analysis, Ultrasonic extraction

Airborne and surface lead represent potential hazards to workers and others, and field-portable methods are sought which may be used to detect and/or monitor this toxic metal in the environment. Recently there has been a significant increase in efforts toward lead hazard reduction in U.S. housing, due to passage of the Lead Hazard Reduction Act of 1992 (Title X) [1] and other federal and state regulations. In order to obtain exposure monitoring results quickly at worksites where lead is a potential occupational hazard, field-portable analytical methods are sought which may be used for on-site assessment of lead exposures. Electroanalytical methods have been evaluated in order to perform on-site trace analysis of lead and other heavy metals, chief among these being stripping techniques [2, 3].

To date, field-portable electroanalytical methods for lead and other heavy metals have been limited mainly to the analysis of water samples [4], which require minimal sample preparation. However, sample preparation techniques for lead in air or in solid matrices such as paint, dust, and soil have required the use of hotplate or microwave acid digestion in the laboratory [5], thereby precluding routine lead analysis in the field. Equipment that can be carried by hand into the field is sought by many potential users of portable analysis instruments.

In this work, an ultrasonic extraction technique, utilizing dilute nitric acid, was used to prepare representative National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) for subsequent lead analysis. Also, laboratory-prepared airborne lead samples collected on cellulose membrane filters were subjected to the ultrasonic extraction procedure. Ultrasonic extraction has been proposed by the U.S. Environmental Protection Agency (EPA) as a viable sample preparation method for bulk samples prior to field-portable colorimetric analysis for lead [6]. After ultrasonic extraction, samples were analyzed for lead content by means of a commercial field-portable, battery-powered anodic stripping voltammetry (ASV) instrument. Based on the results of this study, the protocol described shows promise for the on-site analysis of lead in paint, dust, soil and workplace air.

Ultrasonic extraction is a much simpler sample preparation technique than the currently accepted hotplate or microwave digestion methods, since it does not require concentrated acids nor the use of elevated temperatures and/or pressures to effect the solubilization of lead from environmental samples. Also, ultrasonic extractions can be conducted in a very short time in comparison to laboratory-based strong acid digestions. Hence, ultrasound was chosen in this study as a potential field-based sample preparation procedure for on-site environmental analysis by ASV. Analyses were conducted using a battery-powered, hand-portable ASV instrument (Chemtronix Model PDV 2000).

Samples prepared by ultrasonic extraction for subsequent portable ASV analysis were treated in a similar manner to that described in the EPA Standard Operating Procedure [6]. Weighed amounts of SRMs were added to 50-mL centrifuge tubes, or air filter samples were placed into the tubes with tweezers. Ten mL of 10% nitric acid was then added to each centrifuge tube, and the tubes were capped. Samples were then placed into the ultrasonic bath, and the water within the bath was brought up to a level at least 2.5 cm above the level of liquid inside the centrifuge tubes. The samples were then subjected to ultrasonic energy for 30 min, cooled to room temperature, and diluted to 50 mL with ASTM Type I water [7].

Selected air filter samples were prepared by microwave digestion and then analyzed by flame atomic absorption spectrophotometry (FAAS) in the following manner. The filter samples were transferred to microwave digestion vessels, and 5 mL aliquots of 50% concentrated HNO_3/50% H_2O were pipetted into each vessel, and the vessels were sealed. The samples were then digested by microwave energy (CEM Model MDS 2100), as described in ASTM practice ES 33 [9]. After cooling to room temperature, 20 mL of water was added to each sample, and the samples were shaken and transferred to polypropylene containers. The samples were then analyzed according to NIOSH method 7082 [8] (FAAS, Perkin-Elmer Model 5000).

For portable ASV analyses, the electrolyte solution was prepared in the following fashion: first 117 g NaCl, then 35.5 g L-ascorbic acid, and finally 7.7 g NaOH were added to 400 mL H_2O and dissolved in the above order. This electrolyte is integral

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Table 1. Lead recoveries determined from representative NIST standard reference materials, using ultrasonic extraction in 10% HNO_3 and portable ASV analysis.

SRM	*Number of samples n*	*Percentage recovery* [a]
1579, lead-based paint [b]	11	94.5 ± 5.7
1648, urban dust [c]	12	91.4 ± 3.7
2704, river sediment [d]	12	82.4 ± 7.6

[a] ± values are standard deviations; [b] 11.83% Pb by weight; [c] 0.655% Pb by weight; [d] 0.0161% Pb by weight.

to field-portable stripping analysis, as the L-ascorbic acid serves to scavenge dissolved O_2, which could otherwise interfere with the ASV measurement. Thus it is not necessary to purge the electrolyte solution with an inert gas such as N_2 or He prior to analysis.

The electrochemical cell body and components were comprised of poly-tetrafluorinated ethylene (PTFE), which is inert to inorganic acids and salts. The cell contained a glassy carbon working electrode, an Ag/AgCl (3 M KCl) reference electrode, and a platinum counter electrode. A mechanical stirrer within the electroanalytical cell provided automatic agitation of the cell solution, and a spring-loaded drain plug at the bottom allowed for removal of solution from the cell. Electrolyte solution and sample aliquots were introduced into the electrochemical cell via pipetting through two ports atop the cell. Mercury films were deposited onto the glassy carbon working electrode from 10 ppm $Hg(NO_3)_2$ in H_2O for 5 min at −0.9 V (vs. Ag/AgCl). The glassy carbon electrode was periodically removed from the cell and cleaned gently with a wetted laboratory wipe (Kimwipes).

After being allowed to settle, aliquots of each of the samples prepared as described above were analyzed for lead content by using the portable ASV instrument. Sample solution aliquots of 0.1 mL to 1 mL volume (diluted first, if necessary) were added to 50% H_2O/50% electrolyte within the electrochemical cell; the final solution volume within the cell was 10 mL. All samples were analyzed by using a menu-driven automated ASV procedure, as described below. First the solution was stirred for 5 s, and the lead plated (with stirring) for 60 s at 0.9 V (vs. Ag/AgCl). After a 15 s quiescent period, an anodic sweep to −0.1 V (staircase waveform) was applied and the lead was stripped (with stirring) from the mercury film; the sweeping/stripping step duration was 5 s. The instrument automatically measured the current (in μA) due to the lead oxidation peak at ca. 470 mV. In this work, all data were obtained by measurement of the current at the lead stripping peak potential. If desired, based on input from a standard solution of 100 ppb $Pb(NO_3)_2$, the instrument may report the lead concentration of the cell in ppb. The electrochemical cell was rinsed and stirred (for 5 s) three times with ca. 10 mL of H_2O between each sample run to prevent analyte carryover.

Percent recoveries of lead from NIST SRMs using ultrasonic extraction followed by portable, battery-powered ASV analysis, are summarized in Table 1. The recoveries were computed based on the NIST certified lead contents of the SRMs; these are (in percent lead by weight) 11.83% for SRM #1579, 0.655% for SRM #1648, and 0.0161% for SRM #2704. Amounts of NIST SRM that were weighed out for the recovery study were ca. 0.01 to 0.15 g for SRM #1579, ca. 0.02 to 0.25 g for SRM #1648, and ca. 0.1 to 1.5 g for SRM #2704. Dilution factors used for ASV analysis ranged from 10 for SRM #2704 aliquots to as high as 10 000 for aliquots of SRM #1579; dilution factors for SRM #1648 were intermediate between those used for SRMs #1579 and #2704.

The recoveries of lead from the NIST SRMs are statistically equivalent to those obtained by using hotplate digestion with strong acid solutions [10]. Using 95% confidence limits, *t*-tests of the data revealed that the percent recoveries of lead from each SRM were statistically equivalent to the recoveries determined from NIOSH methods 7082, 7105 and 7300 (nitric acid, hydrogen peroxide and nitric acid/perchloric acid, respectively) [8]. The NIOSH hotplate digestion methods, which utilize concentrated acids and/or 30% H_2O_2 and a hotplate temperature of 140 C, are recognized as being the benchmark digestion techniques for essentially quantitative recoveries of lead from environmental samples [11]. Lead recoveries of 100% can only be achieved with concentrated HF, which enables extraction of lead from otherwise insoluble silicates (which are especially prevalent in SRM #2704). Thus the results of Table 1 indicate that the ultrasonic extraction technique, followed by portable anodic stripping voltammetric determination of lead, gives essentially quantitative recoveries of lead from the three NIST SRMs. The results are somewhat surprising in view of the fact that there was a great deal of undissolved residue remaining after ultrasonic extraction.

Ultrasonic extraction devices offering at least 50 W of power are recommended by the US EPA to achieve acceptable lead recoveries from environmental samples [6]. Also, extraction periods of greater than 30 min do not result in greater recoveries, while extraction times of 15 to 20 min may result in lower recoveries for most environmental matrices [6]. Hence, an extraction time of 30 min seems to be optimum for environmental media of concern here. This time period is certainly of short enough duration to allow for on-site use.

Results from an evaluation of the ultrasonic extraction/portable ASV analysis method using unspiked and spiked samples of water and filter media are summarized in Table 2. Detection limits and quantitation limits were computed using established consensus criteria [12, 13]. Blank (unspiked) and spiked cellulose ester membrane filters were subjected to the same ultrasonic extraction protocol as that described above for NIST SRMs. Sample solution aliquots were then analyzed by portable ASV following dilution to 10 mL (in the electrochemical cell) with a mixture of 50% H_2O and 50% electrolyte solution.

Table 2. Method evaluation parameters for ultrasonic extraction/portable ASV analysis determined from spiked solutions ($n = 6$) of: 1. water and 2. ultrasonically extracted cellulose ester membrane filters. L.O.Q.: limit of quantitation; *m*: slope of calibration line; *b*: *y*-intercept of calibration line; S_y standard deviation of *y*-estimate about the calibration line; *r* correlation coefficient ($n = 6$); I.D.L.: instrumental detection limit; M.D.L.: method detection limit.

Detection limit	*L.O.Q.*	*m* [μA/ppb]	*b* [μA]	S_y [μA]	*r*
1. I.D.L. = 0.7 ppb	2.4 ppb	20.3	14.7	4.9	0.999
2. M.D.L. = 0.09 μg [a]	0.31 μg [a]	18.9	22.0	5.9	0.998

[a] These values were computed from their corresponding concentrations in ppb (0.9 and 3.1 ppb, respectively), accounting for a ten-fold dilution

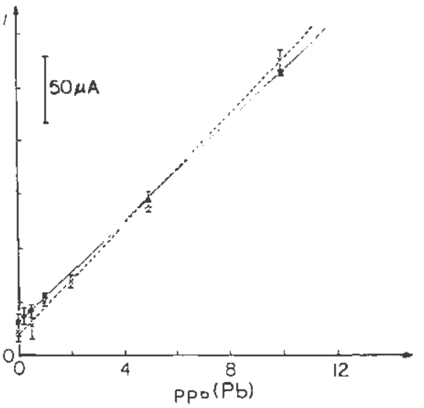

Fig. 1. Calibration curves from portable ASV analysis of low-lead level spiked water (- - -X- - -) and cellulose ester membrane filter (—●—) blanks, following ultrasonic extraction in 10% HNO_3. The error bars are standard deviations computed from repeat runs.

Calibration plots for low-level spikes of the method and water blanks are shown in Figure 1. Spiked solutions ranging from 0.1 to 10 ppb of lead were used to generate the results shown in Table 2 and Figure 1. The correlation coefficients were determined from linear least squares treatments for these low level spiked solutions by measuring the instrumental response (in μA) as a function of the lead concentration (in ppb). The nonzero y-intercept is attributed to background current due to trace lead present in the supporting electrolyte, which was not subtracted from the measured signal.

As can be seen from the results of Table 2, the instrumental detection limit was better than 1 ppb Pb: this is outstanding for a field-portable analysis tool. Assuming a minimum dilution factor of ten, the method detection limit (MDL) was determined to be less than 0.1 μg Pb (Table 2). This value is comparable to the MDL for graphite furnace atomic absorption spectrophotometry (GFAAS) following strong acid hotplate digestion (NIOSH method 7105 [8]). Thus the portable ASV instrument may be used for on-site trace measurements of lead in cellulose membrane workplace air filter samples (in addition to other matrices).

Although the upper limit of the dynamic range of the portable ASV instrument has not yet been evaluated, the plot of instrument response (current) vs. lead concentration was observed to be linear to at least 10 ppm Pb ($r = 0.999$). Relative standard deviations (RSDs) for repeated ASV runs of 10 to 500 ppb solutions ($n = 3$ to 6) were typically better than 1%.

Laboratory-prepared air filter samples containing lead were extracted and analyzed using ultrasound and portable ASV analysis. These laboratory-generated air filters ($n = 10$) were found to contain between ca. 40 and ca. 80 μg Pb/filter; blank filters revealed no detectable lead mass. Relative standard deviations (RSDs) for repeat analyses of filter samples were typically better than 0.5%, and RSDs from data obtained from separately prepared analyte solutions ranged from ca. 0.5% to ca. 5%.

Duplicate laboratory-prepared air filter samples were analyzed by flame atomic absorption spectrophotometry (FAAS; NIOSH method 7082 [8]) following microwave digestion in concentrated HNO_3 [9]. Results from filter samples analyzed by microwave/FAAS are compared to data obtained from samples run by ultrasound/ASV in Figure 2. The slope (1.013) of the calibration line, computed by linear least squares, is very close to unity, and the intercept (−0.47) is near the origin.

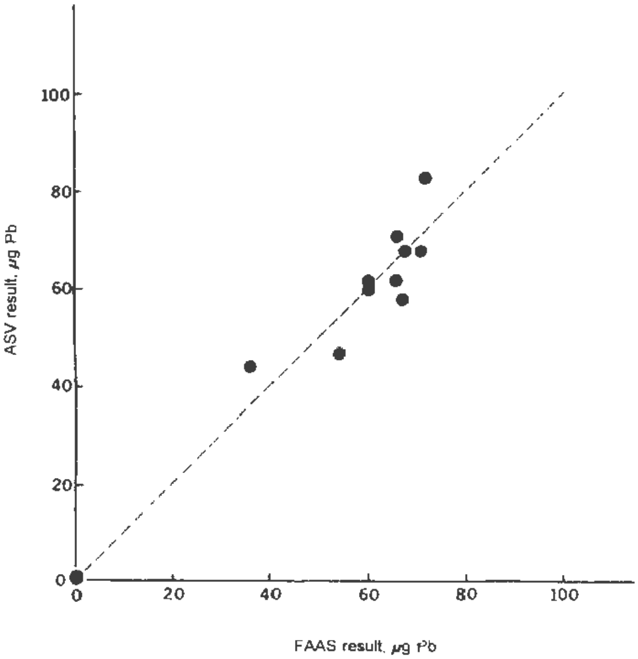

Fig. 2. Plot of results from ultrasonic extraction portable ASV analysis vs. data obtained by microwave digestion FAAS analysis, for laboratory-prepared cellulose ester membrane filter samples. The dashed line indicates unity slope and zero intercept.

Additionally, the correlation coefficient $r = 0.983$, and the standard deviation in the y estimate (μg) about the line $S_y = 5.9$. The RSD for a predicted lead mass of 60 μg/filter is ca. 2%. It can be seen from these figures of merit that the results from the field-portable method compare well to those from the benchmark laboratory method. Accounting for an expected error of ca. 5% in the generation of duplicate lead fume samples, the relative error in the method protocol is less than 5%.

The results summarized above demonstrate that the ultrasonic extraction/portable ASV method is a viable technique for the on-site analysis of workplace air samples. Since the minimum lead mass measured is more than an order of magnitude lower than that expected on the filter when collecting a 1000-L air sample at the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit [14] (8-h time-weighted average = 50 μg/m^3), the method could be used in the field to assess compliance with OSHA regulations regarding workplace airborne lead exposures. Additionally, the method may be employed for on-site monitoring of lead in media that are of concern in the residential lead hazard mitigation arena [15].

In conclusion, ultrasonic extraction of lead from samples such as paint, dust, soil and air, followed by field-portable (i.e., hand-carryable) anodic stripping voltammetry, appears to be a viable protocol for the on-site determination of lead in environmental samples. The use of ultrasound requires an electrical power source, which may be facilitated on-site by means of a generator if no source of electricity is available. Ultrasound may also prove to be a superior laboratory extraction technique compared to hotplate and microwave digestion, owing to its simplicity, time savings, and safety considerations. Obviously, field-portable ASV may also be (and has been [2–4]) used for the trace analysis of lead in water samples; the emphasis here was the evaluation of the method on solid materials and filter media. Since the L-ascorbic acid in the electrolyte serves to reduce dissolved oxygen, there is no requirement to purge the electrolyte solution of O_2 with an inert gas. This is a decided attribute for field portability of the instrumentation, since transportation of compressed gas into the field is by no means routine. Further confirmation of the ultrasonic extraction/portable ASV method is currently underway by means of hotplate digestion and atomic spectrometric analysis, and these results will be published in the near future.

Experimental

The NIST SRMs used were lead-based paint (SRM #1579), urban dust (SRM #1648), and Buffalo River sediment (SRM #2704). Reagent grade nitric acid (Aldrich) and American Society for Testing and Materials (ASTM) Type I [7] deionized water (Millipore purification system) were used for preparation of samples. Mercuric nitrate used for mercury film deposition, and lead nitrate used for preparation of calibration standards, were both reagent grade (Aldrich). Sodium chloride, L-ascorbic acid, and sodium hydroxide (Fisher Biotech) were enzyme grade, tissue culture grade, and molecular biology grade, respectively. Laboratory-prepared air filter samples were collected from lead fumes generated in the National Institute for Occupational Safety and Health (NIOSH) facility in Morgantown, WV. Airborne particulates were collected onto $0.8\ \mu m$ pore size cellulose ester membrane 37-mm filter cassettes (SKC), as described in NIOSH methods for lead in workplace air [8]. Polypropylene 50-mL centrifuge tubes (Falcon), mechanical pipets and micropipets (Eppendorf), and an ultrasonic bath (Sonicor Model SC-150/H) were utilized in sample preparation. SRMs were weighed to ±0.0001 g on a laboratory balance (Mettler Model AE 163).

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