Ultrasonic extraction and portable anodic stripping voltammetric measurement of lead in paint, dust wipes, soil, and air: An interlaboratory evaluation[†]

Kevin Ashley,[*] Ruiguang Song, Curtis A. Esche,[‡] Paul C. Schlecht, Paul A. Baron and Tamara J. Wise

US Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226, USA

Received 7th May 1999, Accepted 12th July 1999

Recent studies have demonstrated the utility of ultrasonic extraction (UE), followed by portable anodic stripping voltammetry (ASV), for the on-site determination of lead in environmental and industrial hygiene samples. The aim of this work was to conduct an interlaboratory evaluation of the UE-ASV procedure, with a goal of establishing estimates of method performance based on results from collaborative interlaboratory analysis. In this investigation, performance evaluation materials (PEMs) with characterized lead concentrations were used for interlaboratory testing of the UE-ASV procedure. The UE-ASV protocol examined has been promulgated in the form of two separate national voluntary consensus standards (one for UE and another for electroanalysis, which includes ASV). The PEMs consisted of characterized and homogenized paints, soils, and dusts (the last of which were spiked onto wipes meeting national voluntary consensus standard specifications), and air filter samples (mixed cellulose ester membrane) generated using characterized paints within an aerosol chamber. The lead concentrations within the PEMs were chosen so as to bracket pertinent action levels for lead in the various sample matrices. The interlaboratory evaluation was conducted so as to comply with an applicable national voluntary consensus standard that can be used to estimate the interlaboratory precision of a given analytical test method. Based on the analytical results reported by the participating laboratories, relative standard deviations (RSDs) for repeatability and reproducibility were computed for three different lead contents of the four PEMs. RSDs for repeatability were 0.019–0.100 for paints; 0.030–0.151 for soils; 0.085–0.134 for dust wipes; and 0.095–0.137 for air filters. RSDs for reproducibility were 0.127–0.213 for paints; 0.062–0.162 for soils; 0.085–0.134 for dust wipes; and 0.114–0.220 for air filters. With the exception of one of the air filter samples and one of the paint samples, the precision estimates were within the ±20% precision requirement specified in the US Environmental Protection Agency National Lead Laboratory Accreditation Program (NLLAP). The results of this investigation illustrate that the UE-ASV procedure is an effective method for the quantitative measurement of lead in the matrices evaluated in this study.

Introduction

Recent studies have demonstrated the utility of ultrasonic extraction (UE), followed by portable anodic stripping voltammetry (ASV), for the determination of lead in environmental and industrial hygiene samples.[1–5] Research has shown that UE-ASV is an effective tool for the determination of lead in paint, dust, soil, air, and other environmental samples. A new National Institute for Occupational Safety and Health (NIOSH) method for the determination of lead in workplace air by UE-ASV has been published.[6] Also, national voluntary consensus provisional standards, which describe procedures for lead extraction and determination in environmental samples, have been promulgated by the American Society for Testing and Materials (ASTM) based on ultrasonication[7] and electroanalysis.[8] The aim of this work was to conduct an interlaboratory evaluation of the UE-ASV method, with a goal of establishing estimates of method performance based on a collaborative interlaboratory analysis. These method performance parameters estimated from interlaboratory analysis can then be used to update the method performance data of the NIOSH method and the ASTM provisional standards for which only intralaboratory data were previously available.

In this investigation, performance evaluation materials (PEMs) with characterized lead concentrations were used for collaborative interlaboratory testing of UE and ASV procedures. The PEMs consisted of characterized and homogenized paints, soils, and dusts (the last of which were loaded onto wipes), and air filter samples generated using characterized paints within an aerosol chamber. The lead contents within the PEMs were chosen to bracket pertinent action levels for lead in the various sample matrices. Duplicate samples of three different concentrations of each of the four PEMs (a total of 24 samples per laboratory) were sent to volunteer laboratories, which were also participants in the Environmental Lead Proficiency Analytical Testing (ELPAT) program.[9]

It was requested that the participating laboratories prepare and analyze the PEMs in accordance with the ASTM provisional standards provided to the laboratories. The interlaboratory evaluation was conducted so as to comply with a pertinent ASTM standard used to determine the interlaboratory precision of a given analytical procedure of interest.

[†] This article was prepared by US Government employees as part of their official duties, and legally may not be copyrighted in the United States of America.

[‡] Present address: Procter & Gamble Co., Miami Valley Laboratories, 11810 E. Miami River Rd., Cincinnati, OH 45252, USA.

Volunteer laboratories were asked to prepare the PEMs by UE in accordance with ASTM PS87,[7] and to analyze the sample extracts using ASV in accordance with ASTM PS88.[8] ASTM PS87 describes procedures for the preparation of paint, dust wipe, soil, and workplace air samples for subsequent lead determination by using UE[10] in dilute (10–25% v/v) nitric acid, while ASTM PS88 gives protocols for the analysis of extracted samples for lead by ASV or potentiometric stripping analysis (PSA).[11] Analytical results from the laboratories were treated statistically in accordance with ASTM E691[12] in order to estimate interlaboratory precision and repeatability. Similar schemes to that described in ASTM E691 have been employed previously to examine laboratory performance data from the ELPAT program.[13,14]

While the intended application of the UE-ASV procedure is for on-site use in the field, it was not deemed feasible at this stage (due to considerations of costs and logistics) to conduct an interlaboratory evaluation in real field situations. Nevertheless, some previous studies have demonstrated the potential efficacy of UE-ASV for on-site measurement of lead in environmental and industrial hygiene samples.[2–4] An aim of this work was to obtain interlaboratory as well as intralaboratory figures of merit for the UE-ASV procedure, so that a benchmark performance of the protocol might be established prior to further testing of the method in on-site situations in the future.

Performance evaluation samples

Paints, soils, and dust wipes

Paint, soil, and dust wipe PEMs consisted of ELPAT secondary reference materials which were prepared by Research Triangle Institute (RTI, Research Triangle Park, NC, USA).[13] Paints, soils and dusts used were collected at various commercial and residential sites in several States. One of the paints selected for this study was known to contain lead chromate. This material was chosen to represent a real-world situation in which the lead is especially difficult to extract from the paint matrix (lead chromate is highly insoluble). After collection, the paint, soil and dust materials were dried, ground, sieved, and homogenized prior to initial laboratory characterizations for lead content.[13] Dusts were spiked onto wipes (Palintest USA, Erlanger, KY, USA) which meet the specifications of ASTM E1792.[15] Ground and homogenized paint and soil samples, and dust wipe samples were characterized for lead content by a reference analytical method, *i.e.*, microwave digestion in concentrated nitric acid and inductively coupled plasma atomic emission spectrometry (ICP-AES).[16]

Air filter samples

Performance evaluation air filter samples were generated from characterized paints at SRI International (Stanford, CA, USA) within an aerosol chamber. The system consisted of a sonic aerosol generator,[17] a chamber which contained the samplers,[18] and a humidifier for minimizing electrostatic effects.[19] Aerosols were generated by sonic agitation of lead-containing paint PEMs ground to less than 10 mm characteristic diameter. One of the aerosols was generated using paint which contained lead chromate. The paint aerosols were collected onto 37 mm diameter mixed cellulose ester (MCE) membrane filters (SKC, Eighty-Four, PA, USA). The calculated relative standard deviation (RSD) in lead concentration within a single batch of air filters was about 0.070, as estimated by lead analysis of representative air samples using NIOSH Method 7105 [hot-plate digestion in nitric acid–hydrogen peroxide and analysis by electrothermal atomic absorption spectrometry (ETAAS)].[20]

Table 1 Nominal lead contents of performance evaluation materials

Material	Nominal lead content Low	Medium	High
Paints	0.15%	0.50%	2.0%
Soils	100 μg g^{-1}	500 μg g^{-1}	3000 μg g^{-1}
Dust wipes	100 μg	200 μg	900 μg
Air filters	35 μg	60 μg	200 μg

Lead contents of PEMs

Characterized PEMs used in this study consisted of three different lead levels for each of the four materials, with nominal lead concentrations as summarized in Table 1. The lead loadings were targeted to bracket pertinent action levels for lead in the respective sample matrices, as was done in interlaboratory studies of ELPAT data.[13,14]

Interlaboratory evaluation of ultrasonic extraction and anodic stripping voltammetry

The UE-ASV procedures, as delineated in the ASTM preliminary standards, are separated into sample preparation[7] and analysis[8] documents. It was desired that these practices be used in the interlaboratory evaluation and that the data forthcoming from the evaluation could be utilized to update the preliminary standards. The analysis document could thereby be revised and submitted as an ASTM full consensus standard test method.

Precision and bias

ASTM full consensus standard test methods require precision and bias data.[21] Precision data are preferably obtained by interlaboratory evaluation in accordance with ASTM Practice E691.[12] Bias data must be estimated by evaluating the performance of the test procedure in question against reference analytical methods, and/or from determination of recoveries from analysis of certified reference materials (CRMs). For estimation of interlaboratory precision, ASTM E691 specifies a minimum of six participating laboratories. Also, this standard recommends a minimum of four samples for each type of matrix, with duplicates of each of the four samples. In this work, for purposes of feasibility, it was decided to use three test materials for each of the four sample matrices, with duplicates of each sample. Thus, each laboratory received a total of 24 PEM samples for analysis by UE-ASV.

Extraction and analysis procedures

As mentioned previously, it was requested that the laboratories prepare the PEMs by UE according to ASTM PS87,[7] and that the extracted PEMs be analyzed for lead content by ASV according to ASTM PS88.[8] The UE procedure (ASTM PS87) calls for the samples to be placed in centrifuge tubes. Dilute nitric acid (10–25% v/v) is then added to the tubes, and the tubes are placed in an ultrasonic bath and sonicated for 30–45 min, depending on the sample matrix. UE in dilute nitric acid acts to extract lead so that it is in a form available for ASV analysis, that is, as dissolved Pb^{2+} ion. In the ASV procedure (as described in ASTM PS88), aliquots of sample extracts previously treated by UE are removed from the centrifuge tubes and placed in sample vials. Supporting electrolyte and oxygen scavenger are added and dissolved thoroughly. The sample aliquots are then analyzed for lead content by ASV using disposable electrodes. All of the disposable ASV electrodes and portable ASV instruments used in this study were manufactured by Palintest (Gateshead, UK).

Statistical treatment of interlaboratory data

Interlaboratory precision of analytical results from the participating laboratories was examined using statistics described in ASTM Practice E691.[12] Repeatability and reproducibility were calculated for each of the three lead levels of each of the test materials. Repeatability is an estimate of within-laboratory variability, and this was calculated by averaging the squares of the standard deviations of within-laboratory results for each sample. Thus, the average within-laboratory variance is the repeatability variance, $(s_r)^2$. Reproducibility is an estimate of the variability of both within-laboratory and between-laboratory results. Reproducibility variance is given by $(s_R)^2=(s_r)^2+(s_L)^2$, where s_L is the standard deviation of the mean value as estimated by the average of all interlaboratory study test results for a given material. Relative standard deviations (RSDs) for repeatability and reproducibility (RSD_r and RSD_R, respectively) are then calculated by dividing the repeatability or reproducibility standard deviation (s_r or s_R) by the mean interlaboratory study test result for a given material. The RSD for a given test material can then be compared with the precision that is desired for the test method under evaluation.

Statistical outlier tests used included Dixon's Q-test[22,23] ($P=0.05$) as well as tests for results outside ±2 standard deviations for pooled data.[24] Outlier tests were conducted on suspect results in cases where suspected outliers could not be identified due to systematic errors owing to procedural mistakes, contamination, or equipment problems. For cases where statistical outliers were identified, data were treated statistically both including and excluding statistical outliers.

Participating laboratories were identified by number to ensure confidentiality.

Results of the interlaboratory study

A total of ten laboratories participated in the interlaboratory evaluation. Not all laboratories analyzed all samples of test material or all matrices. Some laboratories analyzed test materials from only one sample matrix, while others analyzed more than one matrix.

Paint PEMs

Analytical results from individual laboratories participating in the interlaboratory study for paint PEMs are summarized in Table 2. In Table 2, low and medium results from Laboratory #2 were identified as outliers due to a procedural error, and were therefore discarded. (The instrumental sensitivity setting used by Laboratory #2 for low and medium lead level paints was incorrect, which resulted in the reported values being significantly lower than expected.) Overall mean values (interlaboratory means computed from the pooled individual laboratory averages) are close to the nominal target concentrations for lead in paint summarized in Table 1. Variability (as indicated by the RSD) increases with increasing lead content. This runs contrary to the general trend observed in ELPAT data for paints.[13,14] For high results presented in Table 2, statistical outlier tests[22–24] on the data from Laboratory #9 ruled out the identification of these results as statistical outliers (which appeared by initial examination to be low).

Table 2 Paint analysis results from individual laboratories. (Lead concentration in units of per cent. lead by weight.)

	Measured lead content (wt.% Pb)		
Laboratory	Low	Medium	High
1	0.175, 0.174	0.496, 0.481	1.62, 1.14
2	—[a]	—[a]	1.4, 1.5
3	0.19, 0.13	0.56, —[b]	2.29, 2.28
4	0.195, 0.178	0.515, 0.520	2.14, 2.04
5	0.146, 0.132	0.536, 0.560	2.25, 2.17
6	0.181, 0.184	0.564, 0.574	2.16, 2.34
7	0.162, 0.170	0.518, 0.499	2.20, 2.11
8	0.15, 0.16	0.44, 0.43	2.20, 2.20
9	0.146, 0.142	0.364, 0.360	1.29, 1.14
μ^c	0.164±0.017	0.499±0.070	1.93±0.41
RSD[d]	0.107	0.140	0.213

[a]Outlier identified due to procedural error. [b]Sample lost. [c]Overall mean; ±values are standard deviations. [d]Relative standard deviation.

Dust wipe PEMs

Individual laboratory analytical results for dust wipe PEMs are summarized in Table 3. In the results of Table 3, a lone statistical outlier [the low (averaged) result from Laboratory #9] was identified by using Dixon's Q-test (P=0.05) as well as an outlier test for data beyond ±2 standard deviations of the mean value for pooled means. Another outlier due to an equipment malfunction was identified in the results for medium lead content (a medium result for Laboratory #2), and was therefore not included in Table 3. (In this case an electrode gave a very low reading which, when re-checked, was found to be erroneous.) Overall mean values determined for all three lead levels in dust wipes are similar to the nominal values presented for dust wipe PEMs in Table 1. The variabilities (as indicated by the RSDs) are comparable to results from ELPAT for dust wipes.[13,14]

Soil PEMs

Analytical results for soil PEMs are summarized in Table 4. An outlier due to an equipment malfunction was identified in the data of Table 4: a very low reading from Laboratory #2 was found to result from erroneous electrode function. This result, when re-checked, confirmed the erroneous electrode reading, and was therefore not included in the data of Table 4. In the data of Table 4, a statistical outlier (the high average result for Laboratory #5) was identified by using Dixon's Q-test ($P=0.05$). This result was also found to be outside ±2 standard deviations of the mean value for the pooled laboratory means. Overall mean values determined for all three lead concentrations in soils are similar to the nominal values presented for soil PEMs in Table 1. The observed variabilities (as indicated by RSDs) are comparable to results from ELPAT data for soils.[13,14]

Table 3 Dust wipe analysis results from individual laboratories. (Lead content in units of micrograms of lead per sample.)

	Measured lead content/μg Pb per wipe		
Laboratory	Low	Medium	High
1	112, 114	259, 163	981, 806
2	93, 129	—[a], 227	978, 796
3	116, 123	185, 228	711, 922
4	124, 123	265, 237	932, 914
5	118, 106	239, 199	788, 786
6	123, 128	216, 230	981, 948
7	113, 111	204, 230	939, 966
8	105, 109	169, 198	966, 880
9	(43, 79)[b]	211, 209	810, 930
μ^c	116±7; (110±19)[d]	217±18	891±59
RSD[e]	0.060; (0.176)[d]	0.083	0.066

[a]Outlier identified due to procedural error. [b]Identified as a statistical outlier. [c]Overall mean; ±values are standard deviations. [d]Computed including statistical outlier. [e]Relative standard deviation.

Table 4 Soil analysis results from individual laboratories. (Lead concentration in units of micrograms of lead per gram of sample.)

	Measured lead content/μg g^{-1} Pb		
Laboratory	Low	Medium	High
1	—[a]	432, 417	3150, —[b]
2	84, —[b]	468, 466	3184, 3004
3	125, 115	553, 561	2700, 2640
4	80, 126	491, 504	3280, 3170
5	104, 87	497, 371	(1961, 1772)[c]
6	109, 110	517, 550	3222, 3209
7	89, 93	494, 517	3040, 3030
8	108, 83	526, 526	2992, 2985
9	—[a]	516, 568	3292, 3002
μ[d]	100±12	499±48	3066±180; (2993±433)[e]
RSD[f]	0.120	0.096	0.059; (0.148)[e]

[a] Outlier identified due to procedural error. [b] Outlier identified due to equipment malfunction. [c] Identified as a statistical outlier. [d] Overall mean; ±values are standard deviations. [e] Computed including statistical outlier. [f] Relative standard deviation.

Air filter PEMs

Analytical results for air filter PEMs are summarized in Table 5. One laboratory (Laboratory #3) reported extremely high values at all three lead levels. These high results from Laboratory #3 were found to be due to a contamination problem, so the data from this laboratory were discarded. In the data of Table 5, one result [the high (averaged) result from Laboratory #6] was suspected to be a statistical outlier, so outlier tests were carried out. By Dixon's Q-test ($P=0.05$), this result failed the outlier test. However, the value in question was beyond ±2 standard deviations of the overall mean value for pooled mean data, so in this respect the high (average) result from Laboratory #6 was identified as a statistical outlier. The overall mean values for all three lead levels in air filter PEMs are comparable to the nominal values summarized in Table 1. Observed variabilities (as indicated by RSDs) are comparable to results for the other three PEMs (*i.e.*, paint, dust wipes, and soils).

Repeatability and reproducibility

Results for repeatability and reproducibility from all four sample matrices, determined in accordance with ASTM E691,[12] are summarized in Table 6. Statistical outliers were not included in the computations for estimating repeatability and reproducibility for the PEMs. When using ASTM E691, if the calculated value for the repeatability standard deviation (s_r) is less than that for the reproducibility standard deviation (s_R), then the larger value is used and s_r is set equal to s_R. In some cases slight differences may be noted between the data presented in Table 6 *versus* the results given in Tables 2–5. This occurs since the statistical treatment of the data when using ASTM E691 is different, as described in the following. For entries in Table 6, average values are computed from all individual test results for a given matrix at a given lead level, rather than from pooled mean values for the average results from each laboratory (used for the data of Tables 2–5). It can be seen from the results of Table 6 that reproducibility relative standard deviation (RSD$_R$) values, which are measures of interlaboratory precision, range from about 0.06 to approximately 0.22.

Table 5 Air filter analysis results from individual laboratories. (Lead content in units of micrograms of lead per filter sample.)

	Measured lead content/μg Pb per sample		
Laboratory	Low	Medium	High
1	36, 38	51, 45	138, 180
3	—[a]	—[a]	—[a]
4	36, 40	57, 55	167, 207
5	33, 35	44, 51	194, 176
6	47, 42	86, 81	(336, 317)[b]
7	34, 34	69, 73	198, 263
8	40, 36	59, 61	196, 189
9	46, 43	78, 60	275, 236
10	36, 37	47, 56	193, 163
μ[c]	38.3±4.3	60.8±12.8	198±38; (215±55)[d]
RSD[e]	0.112	0.211	0.192; (0.256)[d]

[a] Outlier identified due to contamination problem. [b] Identified as a statistical outlier. [c] Overall mean; ±values are standard deviations. [d] Computed including statistical outlier. [e] Relative standard deviation.

Table 6 Repeatability and reproducibility for paint, dust wipe, soil, and air filter PEMs

Lead level	n	Average	s_r	s_R	RSD$_r$	RSD$_R$
(A) *Paints*—						
Low	8	0.163	0.0163	0.0208	0.100	0.127
Medium	8	0.499	0.0094	0.0705	0.019	0.141
High	9	1.93	0.081	0.410	0.040	0.213
(B) *Dust wipes*—						
Low	8	115	9.8	9.8	0.085	0.085
Medium	9	216	29.0	29.0	0.134	0.134
High	9	891	85.7	85.7	0.096	0.096
(C) *Soils*—						
Low	7	99.8	15.0	16.1	0.151	0.162
Medium	9	499.6	33.9	53.2	0.068	0.107
High	8	3066	91.0	191	0.030	0.062
(D) *Air filters*—						
Low	8	38.3	2.16	4.38	0.056	0.114
Medium	8	60.8	5.78	13.4	0.095	0.220
High	7	198	27.2	38.3	0.137	0.193

Discussion

It is useful to consider the variabilities in the analytical results in light of precision guidelines promulgated for lead test methods. US EPA precision requirements for candidate lead test methods have been described under the auspices of the National Lead Laboratory Accreditation Program (NLLAP).[25] The NLLAP precision requirement for CRMs is for the measured result to fall within ±20% of the certified value for lead content. ASTM E1775 gives guidelines for performance requirements for field-portable lead test methods.[26] For field-based extraction followed by field-portable analysis, the ASTM uncertainty guideline for secondary reference materials such as those used in this study is the same as that specified by the US EPA; that is, the desired precision (as measured by the RSD) is $\leqslant 0.20$.

Within-laboratory precision, as measured by repeatability RSD$_r$, meets the EPA and ASTM precision requirements in all cases (Table 6). RSDs for repeatability were in the following ranges for the respective PEMs: 0.019–0.100 for paints; 0.085–0.134 for dust wipes; 0.030–0.150 for soils; and 0.056–0.137 for air filters. The intralaboratory precision was found to be greater than that reported from ELPAT data,[14] where results from over 400 laboratories were examined statistically. This result is not surprising, since far fewer laboratories participated in this interlaboratory study.

Between-laboratory precision, as measured by reproducibility RSD$_R$, also meets the EPA and ASTM precision figure in 10 out of 12 cases (Table 6). Reproducibility RSDs were found to be in the following ranges for the respective PEMs: 0.127–0.213 for paints; 0.085–0.134 for dust wipes; 0.062–0.162 for soils; and 0.114–0.220 for air filters. The results for reproducibility slightly exceed the ±20%

uncertainty specification in two instances: high lead in paint, and medium lead in air filters (Table 6). RSD_R is generally larger here than values reported from ELPAT rounds, where data from over 400 participating laboratories were examined.[14] It is expected that the estimated values for reproducibility determined here would improve if results from more laboratories had been available. Since relatively few laboratories participated in this study, one or two questionable test results could have caused the reproducibility estimates (RSD_R) to be much larger than they might otherwise have been had a larger number of laboratories participated.

Inclusion of statistical outliers would increase the imprecision for a few other cases (Tables 2–5). Recall that statistical outliers were omitted in computing the results given in Table 6. By including statistical outliers in estimating overall (between-laboratory) precision, in only one additional instance would the ±20% EPA and ASTM precision requirement be exceeded. This occurs for high lead in air, Table 5.

It should be mentioned that in the cases where the ±20% EPA NLLAP/ASTM E1775 precision requirements were exceeded (*i.e.*, for high lead in paint and for medium lead in air), the performance evaluation samples were prepared from paints known to contain lead chromate. Lead chromate containing paints represent a challenging matrix for extraction and analysis for lead content, and have been found to give inconsistent recoveries (by UE-ASV) for lead in real-world chromate paint materials.[4] This suggests that some modification of the extraction technique may be needed in cases where the matrix is suspected to contain chromates, in order to improve precision (*e.g.*, increased extraction time).

For air filter samples, another significant contributor to the overall imprecision is the variability in the generation of the aerosol samples. Recall that the estimated RSD for the aerosol-generated air filter samples as analyzed by a reference method mentioned earlier was approximately ±7%. This contribution to variability must be considered in examining the overall variability determined by interlaboratory analysis. The imprecision inherent in the generation of the air filter PEMs may have caused the overall variabilities to be greater than might otherwise have been expected. Variabilities in the preparation of paint, dust wipe, and soil PEMs are much lower than for air filter PEMs. This is indicative of the greater homogeneity in the other (bulk) PEMs, *e.g.*, paint and dust.[27]

In conclusion, the results of the interlaboratory evaluation of the UE-ASV procedure indicate that the method is effective for the quantitative measurement of lead in the media that were evaluated in this study. Only intralaboratory and interlaboratory precision were investigated statistically here, using ASTM E691 as a guide. Explicit tests of bias were outside the scope of this work. However, biases, which have been measured in other studies,[1,2,5] are expected to be insignificant. Minimal bias is indicated in this study, as the overall mean values determined for the PEMs were in all cases very close to the nominal values. With the exception of two PEMs, all of the interlaboratory precision estimates, as measured by reproducibility (RSD_R), were within the ±20% precision requirement specified by the US EPA NLLAP and ASTM E1775. Estimates of interlaboratory precision for UE-ASV were generally less precise than estimates from ELPAT data, but such results were not unexpected given the much smaller number of laboratories participating in this interlaboratory study.

A potential limitation of this study is that the interlaboratory evaluation of the UE-ASV procedure was not carried out on-site in the field, since it was not deemed feasible to do this. Clearly, interlaboratory as well as intralaboratory variability may be greater in field analysis situations compared with variabilities observed in fixed-site laboratories. A few field investigations of the UE-ASV procedure have been carried out, and performance has been found to be acceptable for quantitative measurement purposes.[2–4] However, it would certainly be of interest to conduct a *bona fide* on-site interlaboratory evaluation if such an effort could be arranged. In any case, the on-site performance of the UE-ASV procedure would not be expected to differ markedly from fixed-site laboratory conditions as long as analyses are carried out in areas that are free from lead contamination.

Acknowledgments

This work was partially supported under the auspices of an AIHA–NIOSH Cooperative Research and Development Agreement (CRADA NIO.C92.001.00). We thank the following laboratories for participating in this study: California Department of Health Services, Berkeley, CA; Corrosion Control Consultants and Labs, Kentwood, MI; Free-Col Laboratories, Meadville, PA; J & L Environmental Services, Elfers, FL; Occupational Health Conservation, Jacksonville, FL; University of Alabama, Tuscaloosa, AL; OSHA Technical Center, Salt Lake City, UT; US Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, MD; and US Army Center for Health Promotion and Preventive Medicine—South, Ft. McPherson, GA. Kenn White and Karl Sieber provided critical reviews of the draft manuscript.

Disclaimer

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

References

1 K. Ashley, *Electroanalysis,* 1995, **7**, 1189.

2 US EPA, *Evaluation of the Performance of Reflectance and Electrochemical Technologies for the Measurement of Lead in Characterized Paints, Bulk Dusts, and Soils* (EPA 600/R-95–093), EPA, Research Triangle Park, NC, 1996.

3 K. Ashley, *Appl. Occup. Environ. Hyg.*, 1998, **13**, 94.

4 K. Ashley, M. Hunter, L. H. Tait, J. Dozier, J. L. Seaman and P. F. Berry, *Field Anal. Chem. Technol.*, 1998, **2**, 39.

5 K. Ashley, K. J. Mapp and M. Millson, *Am. Ind. Hyg. Assoc. J.*, 1998, **59**, 671.

6 *NIOSH Manual of Analytical Methods*, ed. M. E. Cassinelli and P. F. O'Connor, Method No. 7701, NIOSH, Cincinnati, OH, 4th edn., 2nd Suppl., 1998.

7 ASTM PS 87, 'Provisional standard practice for ultrasonic extraction of paint, dust, soil, and air samples for subsequent determination of lead,' in *Annual Book of ASTM Standards*, ASTM, W. Conshohocken, PA, 1998, vol. 04.11.

8 ASTM PS 88, 'Provisional standard practice for determination of lead in paint, settled dust, soil, and air particulate by field-portable electroanalysis,' in *Annual Book of ASTM Standards*, ASTM, W. Conshohocken, PA, 1998, vol. 01.11.

9 C. A. Esche, J. H. Groff, P. C. Schlecht and S. A. Shulman, *Proficiency Analytical Testing and Environmental Lead Proficiency Analytical Testing Programs* [DHHS (NIOSH) Publ. No. 95–104], NIOSH, Cincinnati, OH, 1994.

10 K. Ashley, *Trends Anal. Chem.*, 1998, **17**, 366.

11 J. Wang, in *Laboratory Techniques in Electroanalytical Chemistry,* ed. P. T. Kissinger and W. R. Heineman, Marcel Dekker, New York, 2nd edn., 1996, ch. 24.

12 ASTM E691, 'Standard practice for conducting an interlaboratory study to determine the precision of a test method,' in *ASTM Standards on Precision and Bias for Various Applications*, ASTM, Philadelphia, PA, 4th edn., 1992.

13 P. C. Schlecht, J. H. Groff, A. Feng and R. Song, *Am. Ind. Hyg. Assoc. J.*, 1996, **57**, 1035.

14 P. C. Schlecht, R. Song, J. H. Groff, H. A. Feng and C. A. Esche, *Am. Ind. Hyg. Assoc. J.*, 1997, **58**, 779.

15 ASTM E1792, 'Standard specification for wipe sampling materials for lead in surface dust,' in *Annual Book of ASTM Standards*, ASTM, W. Conshohocken, PA, 1998, vol. 04.11.

16 US EPA, *Evaluation of Hotplate- and Microwave-Based Methods*

for Extracting Lead in Paint, Dust, and Soil with Measurement by Atomic Absorption Spectrometry and Inductively Coupled Plasma Emission Spectrometry (EPA 600/R-94/147), EPA, Research Triangle Park, NC, 1995.

17 D. A. Weyel, M. Ellakkani, Y. Alarie and M. Karol, *Toxicol. Appl. Pharmacol.,* 1984, **76**, 544.

18 T. P. Carsey, *Am. Ind. Hyg. Assoc. J.,* 1987, **48**, 710.

19 P. A. Baron and G. J. Deye, *Am. Ind. Hyg. Assoc. J.*, 1990, **51**, 51.

20 *NIOSH Manual of Analytical Methods*, ed. P. M. Eller and M. E. Cassinelli, Method No. 7105, NIOSH, Cincinnati, OH, 4th edn., 1994.

21 ASTM, *Form and Style for ASTM Standards*, ASTM, Philadelphia, PA, 8th edn., 1989.

22 J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, Wiley, New York, 1984, ch. 3.

23 *Use of Statistics to Develop and Evaluate Analytical Methods*, ed. G. T. Wernimont and W. Spendley, American Association of Official Analytical Chemists, Arlington, VA, 1985, ch. 4.

24 P. C. Meier and R. E. Zund, *Statistical Methods in Analytical Chemistry*, Wiley, New York, 1993, ch. 1.

25 US EPA, *National Lead Laboratory Accreditation Program*, EPA, Washington, DC, 1993.

26 ASTM E1775, 'Standard guide for evaluating the performance of on-site extraction and field-portable electrochemical or spectrophotometric analysis for lead,' in *Annual Book of ASTM Standards*, ASTM, W. Conshohocken, PA, 1998, vol. 04.11.

27 US EPA, *Preparation of Lead-Containing Paint and Dust Method Evaluation Materials and Verification of the Protocol by Round-Robin Analysis* (EPA 600/R-93/235), EPA, Research Triangle Park, NC, 1993.

Paper 9/03685G