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Laboratory and Analytical Method Performance of Lead Measurements in Paint Chips, Soils, and Dusts

The National Lead Laboratory Accreditation Program (NLLAP) recognizes laboratories capable of analyzing lead in paints, soils, and dusts. NLLAP requires successful participation in the Environmental Lead Proficiency Analytical Testing (ELPAT) program. For paint chip analyses, laboratory-to-laboratory variability is about 10% relative standard deviation (RSD) for lead levels near 0.5%, the HUD definition of lead-based paint. For soil analyses, RSDs are about 9 to 10% near relevant federal soil standards and 16% near the lowest state bare soil standard that currently exists. For dust wipe analyses, RSDs range from 10 to 16% for lead levels near relevant HUD standards. Of participating laboratories, 92 to 93% consistently meet ELPAT performance limits. A variety of analytical methods gives similar results. No conclusive significant differences were found among most frequently used hotplate and microwave sample preparation techniques. In addition, several participating laboratories have successfully used ultrasonic extraction methods, a method suitable for use at abatement sites. The three most frequently used instrumental techniques, flame atomic absorption (FAA), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and graphite furnace atomic absorption show no statistically significant differences in ability to meet ELPAT performance limits. However, small statistically significant biases between these methods sometimes occur. The magnitude of biases is less than 5% of the corresponding laboratory mean near relevant federal standards except for lead levels near the lowest HUD lead wipe standard, where biases can be as high as 8%. Other instrumental methods that have been used successfully include ICP-mass spectroscopy, direct current plasma-atomic emission spectroscopy, dithizone spectrophotometry, and anodic stripping voltametry.

Keywords: Environmental Lead Proficiency Analytical Testing program, laboratory-to-laboratory variability, lead measurements, National Lead Laboratory Accreditation Program

The Department of Housing and Urban Development's (HUD's) *Guidelines for the Evaluation and Control of Lead-Based Paint Hazards* recommends the use of Environmental Protection Agency (EPA) National Lead Laboratory Accreditation Program (NLLAP) recognizes laboratories to ensure the consistency and quality of lead measurements in paints, soils, and dusts.(1) NLLAP recognition requires laboratory accreditation with on-site assessment of laboratory operations and continuing successful participation in a proficiency testing program. The NLLAP-recognized proficiency testing program is the Environmental Lead Proficiency Analytical Testing (ELPAT) program. The ELPAT program began in 1992, and after three years of operation has over 400 laboratories from the United States and Canada participating.

The ELPAT program is administered by the American Industrial Hygiene Association (AIHA) in cooperation with the Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health (NIOSH), and the EPA Office of Pollution Prevention and Toxics.(2-4) The program's purpose is to evaluate and improve the performance of laboratories conducting analyses associated with lead abatement. The proficiency test samples are prepared by Research Triangle Institute (RTI) on a quarterly basis using real world paint chips, soils, and dusts. The performance of laboratories and analytical methods is evaluated quarterly at NIOSH and published as columns in the American Conference of Governmental Industrial Hygienist's *Applied Occupational and Environmental Hygiene Journal and* in the *American Industrial Hygiene Association Journal.*(5,6) This study summarizes the performance of laboratories, sample preparation techniques, and instrumental methods over the first three years, 1992 to 1995, of the ELPAT program.

PREPARATION OF PROFICIENCY TEST SAMPLES

The ELPAT program has three main aspects to its operation. First, the samples used for proficiency testing are prepared from real-world samples of paint chips, soils, and dusts. Second, the program is performance-based (i.e., laboratories can choose the analytical method to be used). Third, the program is open to all interested industrial hygiene and environmental laboratories.

RTI collects and prepares the three types of samples used in the ELPAT program. Paint chips are collected from commercial lead abatement contractors, building renovation sites, and demolition sites located in North Carolina, Ohio, and Georgia. Preliminary analysis is made on various bags of collected paint chips to determine the screening values for each. One or more bags of paint chips are ground, milled to a maximum particle size of 120 µm, and blended to produce the final product.(7)

Soils are collected from driplines around older houses, building renovation sites, and industrial sites located in Louisiana, North Carolina, California, New Jersey, and Colorado. Soil samples are dried and sterilized by heating to 325°F for a minimum of 2 hours. Lumps are broken up and then passed through a 2-mm sieve. Finally, the soils are sieved to a maximum particle size of 150 µm. One or more bags of samples may be blended together to prepare the product for final analysis.

Dust wipe samples are prepared from dust collected from households, hotels, motels, and abatement sites in North Carolina. After sterilization by gamma irradiation, the dust is sieved to a maximum particle size of 150 µm. The dust is loaded on individual Whatman No. 40 filters using 100 mg±0.5 mg portions. The loaded filters are then moistened with 0.5 mL of a 3% hydrogen peroxide solution to prevent growth of mold and mildew.(8)

The final prepared samples of paint chips, soils, and dusts on filter paper are loaded into plastic vials and verification is carried out by both RTI and NIOSH laboratories. The verification results must be within ±20% of target values, the relative standard deviations (RSDs) must be less than or equal to 10%, and RTI and NIOSH laboratory results are required to be within ±20% of each other for paint chips, soils, and dust wipes. (RSD is the standard deviation/mean.)

In the initial rounds of the ELPAT program, no preservative was added to the dust wipes; this resulted in mold and mildew growth, which was noticed by some laboratories, even though the dust was sterilized by gamma irradiation. Tests were performed at RTI on various types of preservatives, and it was decided to use 0.5 mL of a 3% hydrogen peroxide solution as a preservative. Laboratories were asked to refrigerate the samples after receipt. They were also asked to analyze the samples as soon as possible after they were received, even though the mold and mildew growth seemed to show no effect on the amount of lead in the dust samples.

The American Society for Testing and Materials (ASTM) has recently developed specification E-1792-96, "Specification for Wipe Sampling Materials for Lead in Surface Dust," which establishes requirements for lead contamination, durability, lead recovery from specified surfaces, acid digestion characteristics, moisture content, size, and thickness for wipes. Plans are to switch to a commercially prepared wipe material that meets the performance criteria.(9) This will probably occur in late 1996.

PROFICIENCY RATING CRITERIA

The evaluation of individual laboratories in the ELPAT program is based on consensus values from reference laboratories and is modeled after the evaluation procedures used in an industrial hygiene proficiency testing program, the Proficiency Analytical Testing program.(10) Reference laboratories are preselected and must meet the following criteria: (1) the laboratory was proficient on the previous round in the ELPAT program for paint chips, soils, and dust wipes, and (2) the laboratory must be accredited by an EPA NLLAP-recognized accrediting organization, the American Association for Laboratory Accreditation (A2LA) or AIHA.(11,12)

After data from reference laboratories are collected and outlier reference laboratory data have been adjusted (Winsorized), the mean ±3 standard deviations of the treated reference laboratory data become the acceptable performance range.(10) Laboratory results are acceptable if they fall within the performance limits. Results falling outside the performance limits are designated as outliers.

Laboratories are rated based on performance in the ELPAT program over the last year (i.e., four rounds) for each lead matrix—paint chips, soil, and dust wipes. The laboratory is proficient for each lead matrix if the following occurs: (1) all four results have been reported, and all are designated as acceptable for the last two consecutive rounds; or (2) three-fourths or more of the results reported in the last four consecutive rounds are designated as acceptable. However, if a laboratory does not report values for the lead matrix on the round being evaluated, the laboratory is not rated. Also, the laboratory is considered probationary for accreditation purposes and is not included on the EPA NLLAP list of approved laboratories for that round and that matrix.

LABORATORY PERFORMANCE

Over the first 12 rounds (three years), 92 to 93% of participating laboratories met the ELPAT proficiency criteria established by NIOSH for paint chips, soils, and dusts. Figures 1 through 3 plot the laboratory-to-laboratory RSDs versus the sample means using ELPAT reference laboratory data. The x-axes are on a log scale to permit the plotting of all points in a single figure, since ELPAT samples test a laboratory's ability to analyze a broad range of concentration levels. A regression line in each plot shows how RSDs increase as lead levels decrease. Laboratory-to-laboratory agreement for paint chips, soils, and dusts among ELPAT reference laboratories using a variety of analytical methods is quite good when compared to the large sample-to-sample variability expected for lead in these matrices.(13–15)

For paint chips (Figure 1), laboratory-to-laboratory variability is about 10% RSD (7 to 12%) for lead levels near 0.5%, the HUD definition of lead-based paint. To determine the potential lead exposures to workers in renovation and remodeling situations, contractors may need to determine if lead is present in the painted surface above the Consumer Product Safety Commission (CPSC) standard of 0.06% lead.(16) In these situations, RSDs near the CPSC standard are about 14%.

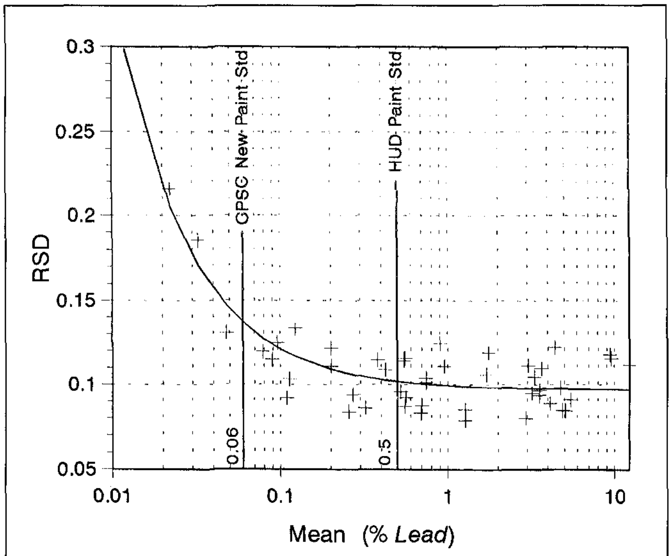

FIGURE 1. Total RSD versus reference mean of paint chip samples in the first 12 rounds

For soils (Figure 2), a variety of standards apply. All soil variability estimates except one estimate from the first round fall near the soil RSD regression line. For decisions concerning the need to remove or pave over soil, or sampling the building perimeter and yard, RSDs are about 9% (7–11%) near the relevant federal bare residential soil standards (2000 and 5000 mg/kg).(1) For samples in play and other high-contact areas (400 μg/m^3 HUD standard), RSDs are higher or about 10% (8–15%).(1) In some instances states have adopted different lead standards than federal standards. Currently Minnesota has the lowest lead in soil standard in the United States. Lead levels near the Minnesota bare soil standard (100 mg of lead/kg) have RSDs of about 16% (13–19%).(17)

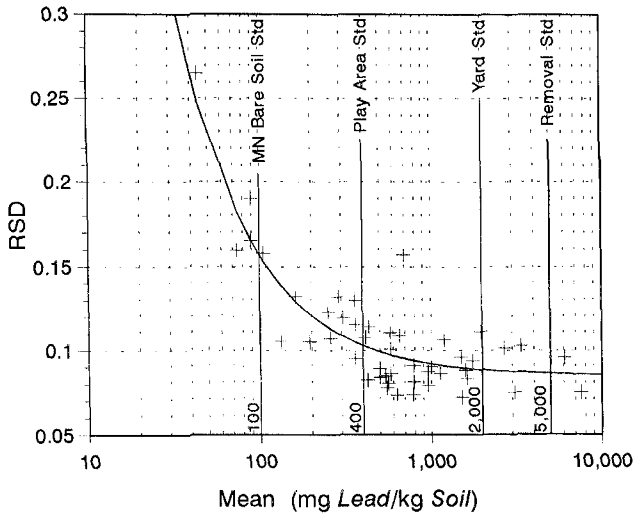

FIGURE 2. Total RSD versus reference mean of soil samples in the first 12 rounds

For dust wipe sampling (Figure 3) RSDs ranged from about 11% (8–12%) for lead levels near the HUD window sill and trough standards (500 and 800 μg/ft^2), to 13.5% (12–17%) near the HUD interior floor standard (100 μg/ft^2) assuming a square foot area is wiped.(1) In other words, laboratory-to-laboratory agreement ranges from about 10 to 16% RSD to make decisions concerning abatement, clearance, or worker air monitoring. This level of laboratory agreement is quite good compared to the larger sample-to-sample variability that one would expect to encounter in sampling painted surfaces, soil sampling, or dust wipe sampling.(13–15)

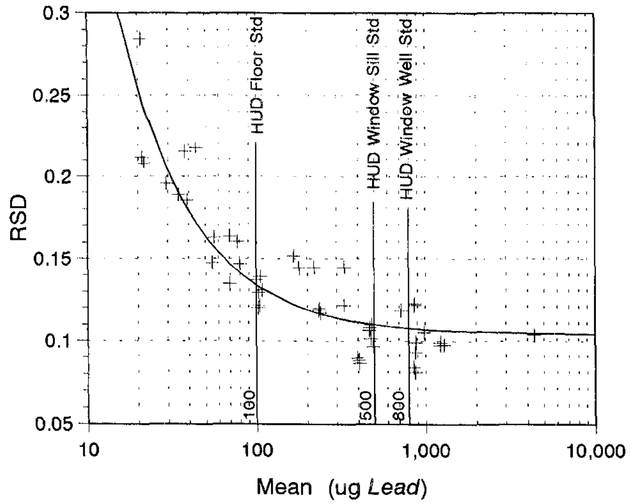

FIGURE 3. Total RSD versus reference mean of dust wipe samples in the first 12 rounds

ANALYTICAL METHODS AND THEIR EVALUATION

Table I shows the sample preparation and instrumental methods used by ELPAT laboratories. Sample preparation is grouped into hotplate, microwave, and all other techniques reported by participants. Hotplate digestion categories are NIOSH 7082/7105 (a nitric acid/hydrogen peroxide digestion method modified from *NIOSH Manual of Analytical Methods, Method 7082 and 7105*);(18) EPA SW846-3050A(19) (an EPA nitric acid/hydrogen peroxide method); and other hotplate techniques. Microwave digestion categories are EPA SW846-3051(20) (a nitric acid digestion method); EPA AREAL(21) (a nitric/hydrochloric acid digestion method from AREAL [RTP-MRDD-037] standard operating procedure); and other microwave techniques. ASTM methods are also available that are based on NIOSH and EPA hotplate and microwave digestion procedures.(22) The "other" category includes nonmicrowave and nonhotplate techniques such as X-ray fluorescence (XRF) sample preparation, leaching techniques, ultrasonic extraction, muffle furnace, and Parr bomb.

TABLE I. Analytical Methods Used in ELPAT Program

Sample Preparation Techniques	Instrumental Methods
Hotplate	flame atomic absorption (FAA)
NIOSH 7082/7105	graphite furnace atomic absorption (GFAA)
EPA SW846-3050A	
other hotplate	ICP-AES
Microwave	laboratory X-ray fluorescence (Lab XRF)
EPA SW846-3051	
AREAL	others
other microwave	
Others	

About 70–80% of the laboratories use NIOSH or EPA hotplate techniques, with more laboratories using EPA hotplate than use NIOSH hotplate. The number of laboratories using NIOSH techniques for each round has decreased, while the number of laboratories using EPA techniques has increased. Similar findings were observed for reference laboratories. Microwave techniques, in particular EPA SW846-3051, are also commonly used. The EPA AREAL method is not commonly used even though the method was specifically developed to optimize analysis of these types of samples.(21)

The predominant instrumental methods used by participating laboratories are flame atomic absorption spectroscopy (FAA) (about 60% of participating laboratories); inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (about 35% of participating laboratories); and graphite furnace atomic absorption spectroscopy (GFAA) (about 2% of participating laboratories for paint chip and soil analyses and about 5% for dust wipe analyses). Only seven laboratories use laboratory XRF methods. Six laboratories used laboratory XRF methods to analyze paint chips and soils samples while only one laboratory used laboratory XRF to analyze all three types of samples. "Other" instrumental methods include ICP-mass spectroscopy (ICP-MS), direct current plasma-atomic emission spectroscopy (DCP-AES), dithizone spectrophotometry, and anodic stripping voltametry (ASV).

Statistical tests are performed on ELPAT data to detect (1) differences in the ability of analytical methods to meet the ELPAT acceptance limits, and (2) differences in bias among the analytical methods. First, a series of Fisher's exact tests (nonparametric tests) are used to examine the differences in the ability to meet ELPAT performance limits among sample preparation techniques and instrumental methods.(23) A criterion is used that classifies participating laboratories into two groups: those that have all acceptable results (no outliers) on the four ELPAT samples of a particular sample type, and those that have one or more nonacceptable results (outliers). Fisher's exact test is then carried out for each ELPAT sample type. No statistically significant differences in the ability of the sample preparation technique and instrumental method combinations to meet ELPAT acceptance limits were detected for paint chip, soil, or dust wipe samples for the first 12 ELPAT rounds.

Second, analysis of variance (ANOVA) procedures are utilized to examine differences in bias among the analytical methods. Both one-way and two-way ANOVAs with Scheffe's multiple comparison test are used to test differences in bias among the principal sample preparation techniques, the principal instrumental methods, and combinations of the two factors.(24) One-way ANOVAs evaluate bias among combinations of sample preparation techniques and instrumental methods while two-way ANOVAs evaluate bias by separating sample preparation technique and instrumental method effects.

To determine relative bias, the general assumptions for ANOVA procedures are verified using a set of predetermined statistical tests. These statistical tests are summarized by the flowchart shown in Figure 4. ELPAT reported results are screened

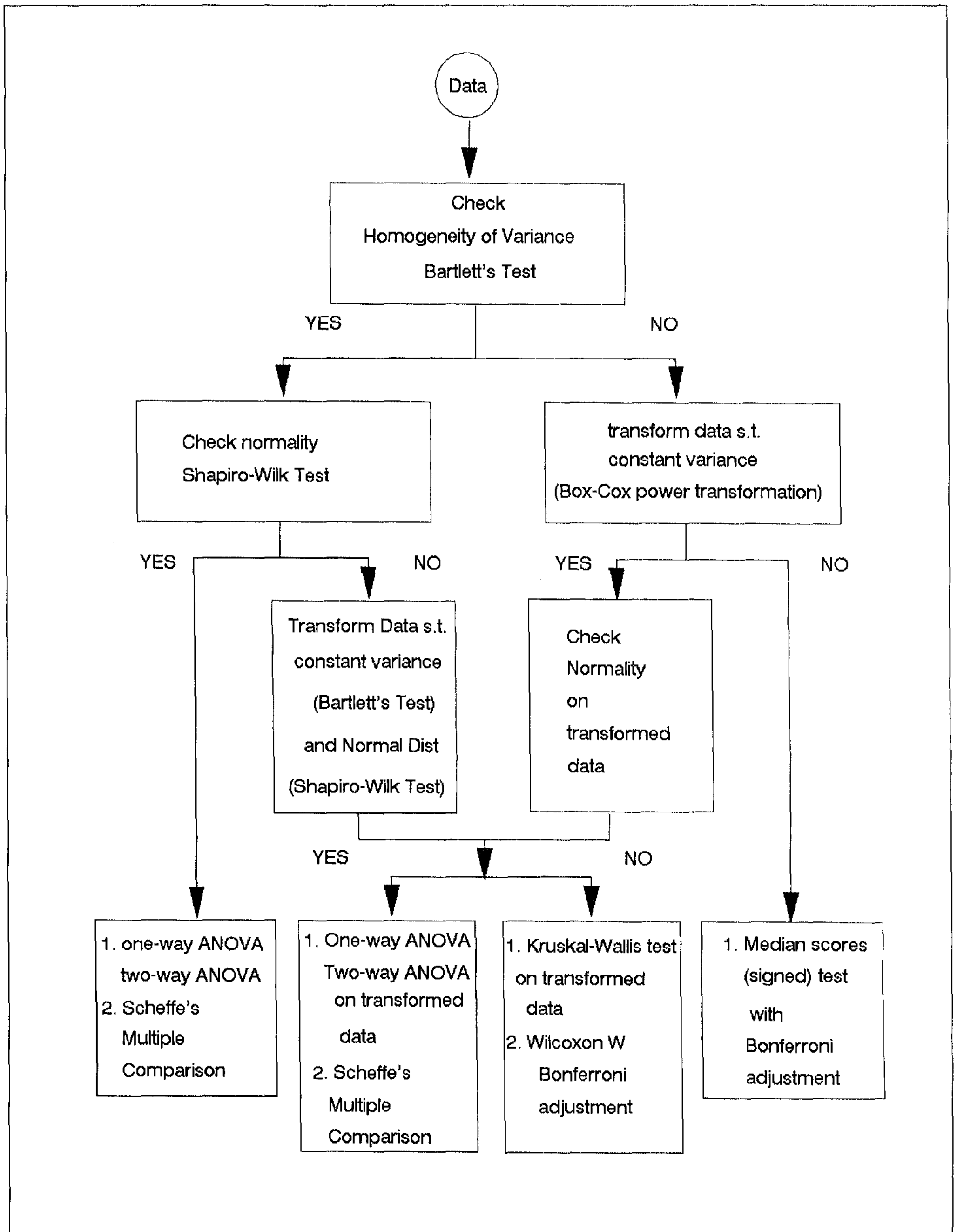

FIGURE 4. ELPAT data analysis strategy

and extreme values removed from the data set using Grubbs test.(25) Analyses are then carried out for each sample type (paint chips, soils, and dust wipes), and each sample (Samples 1, 2, 3, and 4) whenever at least three laboratories pass the Grubb's outlier test.

Data are then tested to check for homogeneity of variance and normality. Bartlett's test is used for testing homogeneity of variances, and the Shapiro-Wilk test is used for testing normality.(26,27) If any one of the two ANOVA assumptions cannot be satisfied, then the median scores test followed by the sign test with Bonferroni adjustment will be used.(28) If either of the ANOVA assumptions are not met, the Box-Cox transformation procedure is applied to the data to determine the appropriate transformation.(29)

If homogeneity of variance or normality is not achieved by transformation, then one of the following two nonparametric tests is used. If transformed data meet the homogeneity of variances, but not the normality assumption, then the Kruskal-Wallis rank sums test followed by the Mann-Whitney-Wilcoxon test with a Bonferroni adjustment is used.(30) If both assumptions cannot be satisfied, then the median scores test followed by the sign test with Bonferroni adjustment is used.(31) If the data (transformed if needed) meet both assumptions, then one-way and two-way ANOVAs with Scheffe's multiple comparison test are done.

ANALYTICAL METHOD PERFORMANCE

Table II summarizes the frequency with which common sample preparation and instrumental methods reported in the program meet ELPAT acceptance limits. Some combinations of sample preparation and instrumental methods shown in Table II are based on data from as few as three laboratories. FAA failure rates range from 3 to 8% over the three-year period depending on the sample technique and sample type. ICP-AES failure rates are similar and range from 0 to 9%. GFAA failure rates are somewhat higher and range from 6 to 40%, but are based on far fewer laboratories. While this may suggest that GFAA has a higher failure rate than FAA or ICP-AES, no statistically significant differences among FAA, ICP-AES, or GFAA instrumental method and various sample preparation technique combinations were found by Fisher's exact test. The overall failure rate for laboratory XRF method is 36 to 37% for paint chip and soil analyses, but because these data are limited, laboratory XRF could not be compared statistically with other methods.

Both one-way and two-way ANOVA analyses were performed for each sample within each round. One-way ANOVA checked bias among combinations of sample preparation and instrumental methods. Two-way ANOVAs separate sample preparation and instrumental effects. Since the results of one-way ANOVA tests are consistent with the results of two-way ANOVA tests, only the results of two-way ANOVAs are discussed and summarized in Table III.

To perform ANOVA, normality of data and homogeneity of variances are verified. Two of the 48 paint chip samples (4%) provided to participating laboratories during the three-year period had nonhomogeneous variances. This indicates that there may occasionally be differences in laboratory-to-laboratory variability among the common analytical methods used by participants. However, subsequent inspection and plotting of analytical method variances revealed no pattern in variability differences. Two-way ANOVA attributed bias to sample preparation for 1 out of 48 soil samples (2%); however, a subsequent Scheffe's multiple comparison test could not ascertain which sample preparation methods were different. Therefore, the evidence of laboratory-to-laboratory variability differences among the analytical methods and bias among sample preparation techniques is both very limited and inconclusive.

However, evidence that bias exists among instrumental methods is extensive and conclusive. Significant differences in the average reported lead value by the three most frequently used

TABLE II. Numbers of Analyses Meeting ELPAT Performance Limits (Rounds 1–12)

			Paint Chips (%)				Soil (mg/kg)				Dust wipes (µg)			
			Accceptable		Failures		Acceptable		Failures		Acceptable		Failures	
Instrument	Digestion	Method	N^A	%	N	%	N	%	N	%	N	%	N	%
FAA	hotplate	NIOSH-7082/7105	1810	93	126	7	1026	95	58	5	2535	95	133	5
		EPA-SW846-3050A	3072	92	268	8	3584	93	268	7	2342	93	174	7
	microwave	EPA AREAL	66	92	6	8	84	95	4	5	58	97	2	3
		EPA-SW846-3051	399	96	17	4	397	95	23	5	302	97	10	3
Subtotal			5347	93	417	7	5091	94	353	6	5237	94	319	6
GFAA	hotplate	NIOSH-7082/7105	44	73	16	27	24	60	16	40	101	81	23	19
		EPA-SW846-3050A	100	78	28	22	159	85	29	15	250	92	22	8
	microwave	EPA-SW846-3051	18	90	2	10	35	88	5	13	49	88	7	13
Subtotal			162	78	46	22	218	81	50	19	400	88	52	12
ICP-AES	hotplate	NIOSH-7082/7105	474	93	38	7	312	93	24	7	689	94	43	6
		EPA-SW846-3050A	2407	93	185	7	2457	92	215	8	1980	92	164	8
	microwave	EPA AREAL	107	92	9	8	72	100	0	0	76	95	4	5
		EPA-SW846-3051	426	94	26	6	411	91	41	9	343	93	25	7
Subtotal			3414	93	258	7	3252	92	280	8	3088	93	236	7
Lab XRF	none	none	76	63	44	37	56	64	32	36	4	50	4	50
Total			8999	92	765	8	8617	92	715	8	8729	93	611	7

^A N = number of ELPAT samples

TABLE III. Analytical Method Bias (Two-Way ANOVA with p< 0.01)

Matrix	Round	Sample Number	Reference Value	Max.-Min. in Mean	Bias
Paint chip	2	1	0.20%	0.02%	ICP-AES< FAA
	2	3	0.38%	0.03%	ICP-AES< FAA
	4	1	0.20%	0.01%	ICP-AES< FAA
	7	2	0.11%	0.01%	ICP-AES< FAA
	7	3	0.27%	0.01%	ICP-AES< FAA
	8	1	0.32%	0.02%	ICP-AES< FAA & GFAA
	8	3	0.08%	0.006%	ICP-AES< GFAA & FAA
	9	2	0.05%	0.008%	ICP-AES< FAA
	10	1	0.11%	0.006%	ICP-AES< FAA
	11	2	0.26%	0.02%	ICP-AES< FAA
	11	4	0.69%	0.04%	ICP-AES< FAA
	12	2	0.12%	0.01%	ICP-AES< FAA
Soil[A]	3	4	1196 mg/kg	58 mg/kg	ICP-AES< FAA
	5	3	581 mg/kg	28 mg/kg	sample preparation[B]
	8	4	792 mg/kg	75 mg/kg	ICP-AES< FAA & GFAA
	11	1	259 mg/kg	30 mg/kg	ICP-AES< FAA & GFAA
	12	1	562 mg/kg	11 mg/kg	ICP-AES< FAA
Dust wipe	2	4	44 µg	5.3 µg	ICP-AES< GFAA & FAA
	3	1	35 µg	6.6 µg	GFAA & ICP-AES < FAA
	3	2	221 µg	26.0 µg	ICP-AES< GFAA & FAA
	4	3	80 µg	6.9 µg	ICP-AES< GFAA & FAA
	5	2	39 µg	6.7 µg	ICP-AES< FAA & GFAA
	5	4	78 µg	7.4 µg	ICP-AES< FAA & GFAA
	6	2	100 µg	25.0 µg	GFAA< ICP-AES & FAA
	6	3	988 µg	150.0 µg	GFAA< ICP-AES & FAA
	8	2	105 µg	8.0 µg	ICP-AES< FAA & GFAA
	8	4	242 µg	24.0 µg	ICP-AES< FAA & GFAA
	12	4	236 µg	15.0 µg	ICP-AES & GFAA< FAA

[A] Only one incidence was found that the difference among sample preparation techniques was significant. This evidence was not enough to allow a conclusion to be drawn.

[B] EPA-SW846-3050/3050A hotplate technique < EPA-SW846-3051 microwave and NIOSH-7082 hotplate techniques

instrumental methods (FAA, ICP-AES, and GFAA) were found. ICP-AES gave statistically lower results than FAA on about one-fifth of the samples. GFAA gave significantly different results from either ICP-AES or FAA on about 8% of the samples, but sometimes GFAA results were higher and other times lower than ICP-AES or FAA. To investigate whether the biases found by ANOVA were due to differences in the specific paint, soil, or dust matrices used on a particular round or analytical factors that may be specific to a particular sample, or were inherent in all analyses reported, plots of relative bias were constructed. No consistent pattern of GFAA bias could be identified, but there was a consistent pattern of bias for ICP-AES and FAA on all three sample types. Figure 5 plots the relative bias between FAA and ICP-AES for all 48 paint chip samples, both those demonstrating statistically significant differences by ANOVA as shown in Table III, and those that do not. The plot shows a consistent trend of bias with ICP-AES giving lower results than FAA at low lead concentrations and higher results when lead concentrations are above about 3% lead. A similar plot of soil relative bias, Figure 6, shows a consistent bias at all lead concentrations of interest, with ICP-AES generally giving 5% or less lower results than FAA. A plot of dust wipe relative bias, Figure 7, shows a consistent pattern of bias, with ICP-AES giving lower results than FAA that increase as lead concentrations decrease.

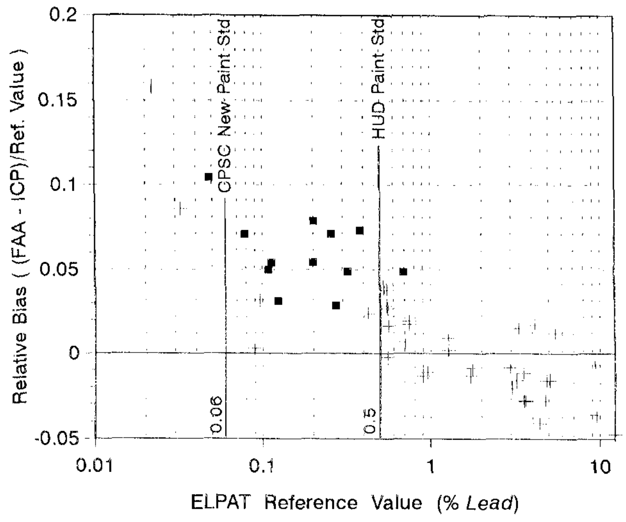

FIGURE 5. Differences in means of FAA and ICP-AES for paint chip samples in the first 12 rounds. Significant differences detected by two-way ANOVA are marked by ■ and listed in Table III.

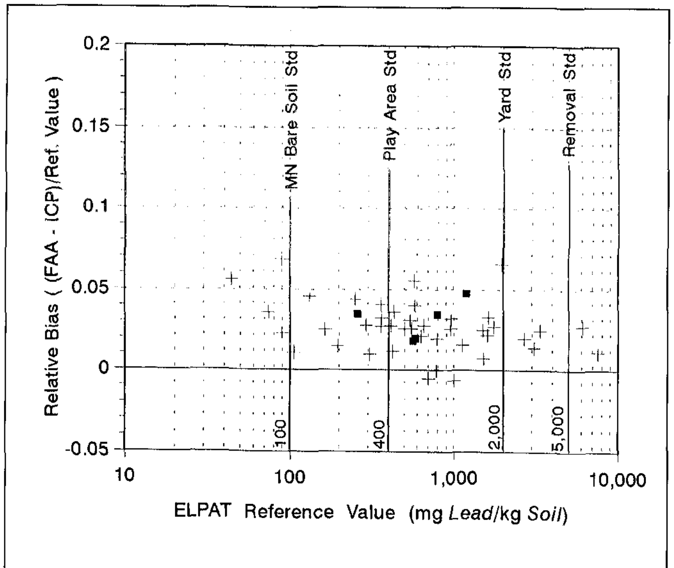

FIGURE 6. Differences in means of FAA and ICP-AES for soil samples in the first 12 rounds. Significant differences detected by two-way ANOVA are marked by ■ and listed in Table III.

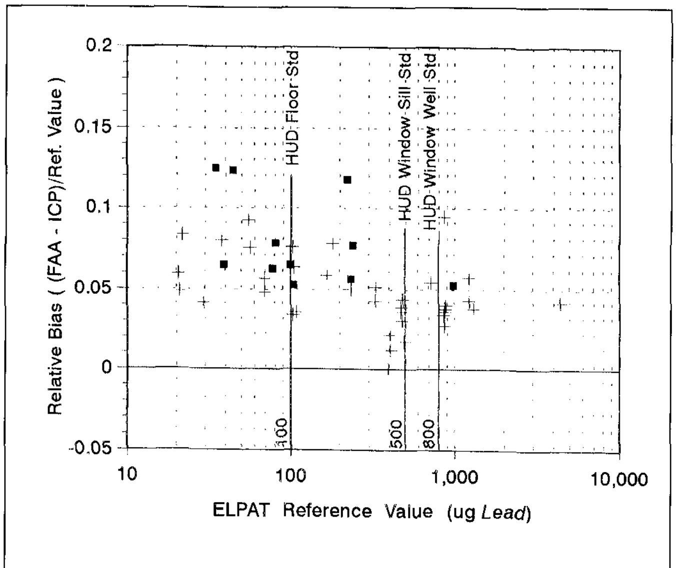

FIGURE 7. Differences in means of FAA and ICP-AES for dust wipe samples in the first 12 rounds. Significant differences detected by two-way ANOVA are marked by ■ and listed in Table III.

DISCUSSION

Most participating laboratories use concentrated acid hotplate and microwave digestions, which theoretically should extract all lead except lead bound in crystal silicate structures. Concentrated acid digestions are generally referred to as "total" lead digestion techniques. These may include nitric acid, nitric acid/hydrogen peroxide, hydrochloric acid, and aqua regia digestions. No participating laboratory reported using hydrofluoric acid (HF), which theoretically extracts all lead. However, some National Institute for Standards and Technology (NIST) Standard Reference Materials (SRMs) have occasionally been used as source materials for the ELPAT program. True "total" digestion methods using either HF or perchloric acid with hydrochloric and nitric acids and analysis by isotope dilution thermal ionization mass spectrometry reported by NIST is generally 4% higher than the reference laboratory mean reported in the ELPAT program.(32,33)

"Other" techniques include nonmicrowave and nonhotplate techniques such as laboratory X-ray fluorescence sample preparation, ultrasonic extraction, and leaching techniques. Laboratory XRF sample preparation generally involves minimal sample preparation such as sieving to remove large particles. Ultrasonic extraction methods using 10 to 25% nitric acid have been published by EPA and NIOSH and are under evaluation at NIOSH for use in the field with field portable instrumentation.(34,35) Leaching techniques use dilute acids and are generally designed to approximate the amount of lead that is "biologically" available. Some laboratories may be required by clients or state regulation (e.g., Minnesota and Maryland) to use leaching methods, but few use leaching methods in the ELPAT program because of a concern that their performance is rated against reference laboratories that use "total" lead digestion techniques. A useful literature review and brief discussion of these sample preparation methods are contained in an EPA document on sampling house dust for lead.(36)

About 7 to 8% of reported results fail to meet ELPAT performance limits on a given sample type and round. Over the first three years no statistically significant differences were found among the most frequently used hotplate and microwave sample preparation techniques in their ability to meet ELPAT performance limits. However, a wide variety of sample preparation methods and an even wider variety of sample preparation modifications may be used by participating laboratories. This makes categorizing sample preparation techniques and studying their effects difficult to perform on ELPAT data, and important differences among sample preparation techniques are easily confounded.

Several participating laboratories on recent rounds successfully used ultrasonic extraction techniques. While the data on ultrasonic extraction performance are currently too limited to permit comparison for statistical differences with other sample preparation techniques, comparisons should be possible in the near future as NLLAP is expanded to cover field portable methods and the use of quantitative field methods increases.

Occasionally laboratories use leaching techniques in the program. However, leaching technique data are too limited and the variety of leaching methods too great for statistical comparison with "total" lead extraction techniques. It is doubtful that the ELPAT program will be able to provide definitive information on leaching methods until information on the comparison of leaching methods versus "total" lead extraction methods using ELPAT or similar reference materials is published. Most participating commercial laboratories would want some definitive information on leaching method recoveries to be assured that use of such methods would not result in low lead recoveries and loss of NLLAP recognition.

The most frequently used instrumental techniques, FAA and ICP-AES, have few ELPAT outliers and show no statistically significant differences in ability to meet ELPAT performance limits. GFAA has a higher outlier frequency. While this higher frequency may appear to be important, the frequency of GFAA outliers is not statistically different from FAA or ICP-AES and is based on a small number of laboratories using GFAA for paint chip and soil analyses, the two matrices with the highest GFAA outlier frequencies.

Other instrumental methods successfully used on all three sample types by one or more participating laboratories include ICP-MS, DCP-AES, dithizone spectrophotometry, and ASV. However, data are too few to make statistical comparisons for these instrumental methods. Laboratory XRF has been used by several participants on paint chip and soil matrices, but laboratory XRF fails to meet ELPAT performance limits about one-third of the time. For the three-year period, insufficient data are available to make statistical comparisons of laboratory XRF methods to other methods. Given that an EPA collaborative test of hotplate and microwave digestion also reported a poor comparison,(21) research to resolve the differences between laboratory XRF and instrumental methods that involve "total" lead digestion methods, or a fundamental understanding of bias, is needed to have confidence that laboratory XRF gives comparable results to other methods.

Over the first 12 rounds, i.e., three years, NIOSH ELPAT bias studies found evidence of bias among the principal instrumental methods used by participating laboratories for all three sample types: paint chips, soils, and dust wipes. ICP-AES consistently gave lower results than FAA for all three sample types except at lead concentrations for paint chips above 2% lead. GFAA also demonstrated bias relative to both ICP-AES and FAA occasionally, but no consistent pattern of GFAA bias was identified.

The FAA/ICP-AES bias found in this study is consistent with the 3 to 18% bias found by RTI in an EPA-sponsored collaborative test.(21) In the EPA collaborative test, it was determined that some FAA laboratories failed to perform background corrections that one would expect to result in a positive bias, and some ICP-AES laboratories failed to take matrix effects into account that one would expect to result in a negative bias. NIOSH does not follow up with participating laboratories to determine if each one has performed all steps of the analytical method. However, NIOSH has recommended to both cooperating accrediting organizations that FAA background correction and ICP-AES matrix minimization procedures should be emphasized regardless of whether the applicant laboratory meets ELPAT performance limits or not. Since only about a fifth of the ELPAT participating laboratories have been accredited by the end of the three-year period of this study, it is premature to determine if such efforts will reduce instrumental method bias in the program.

CONCLUSION

The performance of almost 400 laboratories in the ELPAT program demonstrated that laboratory-based analysis of lead in paints, soils, and dusts can support compliance decisions using current federal and state lead guidelines and standards associated with lead inspections, lead risk assessment, and lead abatement. Over a three-year period, 92 to 93% of ELPAT participating laboratories met proficiency test performance criteria established by NIOSH for NLLAP recognition for paint chip, soil, and dust wipe analyses. For paint chip analysis, laboratory-to-laboratory variability was about 10% RSD near the HUD definition of lead-based paint of 0.5% lead, and about 14% RSD at 0.06% lead, a lead level that sometimes is used to determine whether air monitoring of workers is required in lead abatement, renovation, or remodeling. For soils, laboratory-to-laboratory variability ranged from about 9% at the highest applicable federal standard (5000 mg/kg) to about 16% at the current lowest state standard (the Minnesota Bare Soil standard of 100 mg/kg). For dust wipe sampling, laboratory-to-laboratory variabilities ranged from about 11% for lead levels near HUD window sill and well standards to about 13.5% RSD for levels near HUD interior floor standards assuming a square foot area is wiped.

Sufficient data are available to demonstrate the ability of a variety of hotplate and microwave digestion techniques and instrumental methods (FAA, GFAA, and ICP-AES) to meet ELPAT performance limits consistently. While sufficient data are not available to make statistical comparisons, the performance of some other sample preparation techniques such as ultrasonic extraction and other instrumental methods (ICP-MS, DCP-AES, dithizone spectrophotometry, and ASV) have been successfully used by one or more laboratories in the program.

The evidence of differences in laboratory-to-laboratory variability or bias among sample preparation techniques is very limited and inconclusive. While this study has not shown statistically significant differences in bias among various hotplate and microwave digestion techniques, the wide variety of sample preparation techniques and modifications of sample techniques could confound important sample preparation bias.

Small bias among the principal instrumental methods (FAA and ICP-AES) exists, with FAA giving higher results than ICP-AES at lead levels near relevant federal and state standards. The magnitude of these biases ranges from 7 to 11% near the CPSC standard of 0.06% lead for new paints to 1 to 2% near the soil removal standard of 5000 mg/kg.(16) Because these biases are consistent with an EPA-sponsored collaborative test conducted by RTI, it is suspected that the bias among the principal instrumental methods used by laboratories is at least in part the result of some laboratories using FAA not performing background corrections and laboratories using ICP-AES not performing matrix effect minimization steps. Therefore, NIOSH has recommended to A2LA and AIHA that these factors need to be emphasized during the review of applications for accreditation and during on-site laboratory assessments for NLLAP recognition.

Small bias among GFAA instrumental methods with FAA and ICP-AES methods for paint chip, soil, and dust wipe analyses sometimes occurred, but no consistent pattern of GFAA bias could be determined in this study.

REFERENCES

1. **U.S. Department of Housing and Urban Development (HUD):** *Guidelines for the Evaluation and Control of Lead-Based Paint Hazards in Housing.* Washington, DC: HUD, June 1995.

2. **American Industrial Hygiene Association (AIHA) and National Institute for Occupational Safety and Health (NIOSH):** *Cooperative Research and Development Agreement (CRADA) Between the American Industrial Hygiene Association (AIHA) and the National Institute for Occupational Safety and Health (NIOSH)* [CRADA NIO.C92.001.00]. Fairfax, VA: AIHA; and Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, NIOSH, 1992.

3. **U.S. Environmental Protection Agency (EPA) and National Institute for Occupational Safety and Health (NIOSH):** *Memorandum of Understanding,* project officers J.J. Breen (EPA), J.V. Scalera (EPA), and P. Schlecht (NIOSH) [MOU no. PW75935570-01-0]. Washington, DC: EPA, Office of Pollution Prevention and Toxics; and Atlanta, GA: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, NIOSH, 1992.

4. **National Lead Laboratory Accreditation Program:** *Model Memorandum of Understanding (MOU),* collaborative effort among U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics; Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering; and Accreditation Organizations, 1993.

5. **Schlecht, P.C. and J.H. Groff:** ELPAT program: background and current status. *Appl. Occup. Environ. Hyg. 11(1)*:10–16 (1996).

6. **Groff, J.H. and P.C. Schlecht:** ELPAT program report: background and current status (October 1995). *Am. Ind. Hyg. Assoc. J. 57*:208–215 (1996).

7. **Binstock, D.A., E.E. Williams, J.D. Neefus, and W.F. Gutknecht:** *Standard Operating Procedure for Preparation of Method Evaluation Materials for Lead in Paint,* (EPA 600/R-94/132). Research Triangle Park, NC: U.S. Environmental Protection Agency, 1994.

8. **Binstock, D.A., E.D. Estes, E.E. Williams, J.D. Neefus, et al.:** *Standard Operating Procedure for Preparation of Method Evaluation Materials for Lead in Dust,* (EPA 600/R-94/146). Research Triangle Park, NC: U.S. Environmental Protection Agency, 1995.

9. **American Society for Testing and Materials (ASTM):** *ASTM E1792-96 Standard Specification for Wipe Sampling Materials for Lead in Surface Dust.* Philadelphia, PA: ASTM, 1996.

10. **National Institute for Occupational Safety and Health (NIOSH):** *Laboratory Evaluations and Performance Reports for the Proficiency Analytical Testing (PAT) and Environmental Lead Proficiency Analytical Testing (ELPAT) Programs,* (DHHS/NIOSH pub. no. 95-104). Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, NIOSH, 1995.

11. **American Association for Laboratory Accreditation (A2LA):** *A2LA Environmental Lead Program Requirements.* Gaithersburg, MD: A2LA, 1992.

12. **American Industrial Hygiene Association (AIHA):** *AIHA Environmental Lead Program Policies.* Fairfax, VA: AIHA, 1992.

13. **Sussell, A.L., A. Weber, D. Wild, D. Wall, et al.:** An evaluation of airborne and surface lead concentrations from preliminary cleaning of a building contaminated with deteriorated lead-based paint. In *Lead in Paint, Soil, and Dust: Health Risks, Exposure Studies, Control Measurement Methods, and Quality Assurance,* M.E. Beard and S.D. Allen Iske, eds. (STP 1226) Philadelphia, PA: ASTM, 1995. pp. 145–161.

14. **Small, M., A. Nunn, B. Forslund, and D. Daily:** Source attribution of elevated soil lead near a battery recycling site. *Environ. Sci. Technol. 29(4)*:883–895 (1995).

15. **U.S. Environmental Protection Agency (EPA):** *Sampling House Dust for Lead-Basic Concepts and Literature Review,* (EPA 747-R-95-007). Washington, DC: EPA, 1995. pp. 4-1, 5-9.

16. "Ban of Lead-Containing Paint and Certain Consumer Products Bearing Lead-Containing Paint," 42 *Fed. Reg.* 44199; codified at 16 CFR 1303.1–1303.5, 1977.

17. **Minnesota Pollution Control Agency (MPCA):** *Soil Lead Report to the Minnesota State Legislature.* St. Paul, MN: MPCA, 1987. p. A10.

18. **National Institute for Occupational Safety and Health (NIOSH):** Methods 7082 and 7105. In *NIOSH Manual of Analytical Methods,* 4th ed., P.M. Eller, ed. (DHHS/NIOSH pub. no. 94-113). Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, NIOSH, 1994.

19. **U.S. Environmental Protection Agency (EPA):** Method SW846-3050A, acid digestion of sediments, sludges and soils (metals). In *U.S. EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Method SW846,* 3rd ed. Washington, DC: EPA, 1990.

20. **U.S. Environmental Protection Agency (EPA):** Method SW876-3051, microwave assisted acid digestion of sediments, sludges, soils and oils (metals). In *U.S. EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Method SW846,* 3rd ed. Washington, DC: EPA, 1990.

21. **Binstock, D.A., D.L. Hardison, P.M. Grohse, and W.F. Gutknecht:** *Standard Operating Procedures for Lead in Paint by Hotplate- or Microwave-based Acid Digestion and Atomic Absorption or Inductively Coupled Plasma Emission Spectrometry,* (EPA 600/8-91/213). Research Triangle Park, NC: U.S. Environmental Protection Agency, 1991. Available from NTIS, Springfield, VA (PB 92-114172).

22. **American Society of Testing and Materials (ASTM):** *ASTM Standards on Lead-Based Paint Abatement in Buildings.* Philadelphia, PA: ASTM, 1994.

23. **Fleiss, J.:** *Statistical Methods for Rates and Proportions.* 2nd ed. New York: John Wiley & Sons, 1981. pp. 24–25.

24. **Neter, J., W. Wasserman, and M.H. Kutner:** *Applied Linear Statistical Models,* Boston, MA: Irwin, Inc., 1989. pp. 141–151 614–617.

25. **Barnett, V. and T. Lewis:** *Outliers in Statistical Data.* New York: John Wiley & Sons, 1979. pp. 94–95.

26. **Milliken, G.A. and D.E. Johnson:** *Analysis of Messy Data,* vol. 1. New York: Chapman & Hall, 1992. pp. 18–19.

27. **Shapiro, S.S. and M.B. Wilk:** An analysis of variance test for normality (complete samples). *Biometrika* 52:591–611 (1965).

28. **Lehmann, E.L. and H.J.M. D'abrera:** *Nonparametrics Statistical Methods Based on Ranks.* Oakland, CA: Holden-Day, Inc., 1975. pp. 6, 125–132.

29. **Neter, J., W. Wasserman, and M.H. Kutner:** *Applied Linear Statistical Models—Regression, Analysis of Variance and Experimental Designs,* 3rd ed. Burr Ridge, IL: Irwin, 1990. pp. 149–151, 614–617.

30. **Hollander, M. and D.A. Wolfe:** *Nonparametric Statistical Methods.* New York: John Wiley & Sons, 1973. pp. 27–33.

31. **SAS Institute Inc.:** *SAS/STAT User's Guide, Version 6,* 4th ed., vol. 2. Cary, NC: SAS Institute, 1993. pp. 1195–1203.

32. **National Institute of Standards and Technology (NIST):** *Certificate of Analysis—Standard Reference Material 2582—Powdered Paint (nominal 200 mg/kg lead).* Gaithersburg, MD: NIST Standard Reference Material Program, 1996.

33. **National Institute of Standards and Technology:** *Certificate of Analysis—Standard Reference Material 2589—Powdered Paint (high lead concentration).* Gaithersburg, MD: NIST Standard Reference Material Program. [In preparation]

34. **U.S. Environmental Protection Agency (EPA):** *Standard Operating Procedure for the Field Analysis of Lead in Paint, Soil, and Dust by Ultrasonic Acid Digestion and Colorimetric Measurement,* (EPA 600R-93/200). Research Triangle Park, NC: EPA, 1993.

35. **Ashley, K.:** Ultrasonic extraction and field-portable anodic stripping voltammetry of lead from environmental samples. *Electroanalysis 7(12)*: 1189–1192 (1995).

36. **U.S. Environmental Protection Agency (EPA):** *Sampling House Dust for Lead-Basic Concepts and Literature Review,* (EPA 747-R-95-007). Washington, DC: EPA, 1995. pp. 6–2; 6–3.