A comparison of methods and materials for the analysis of leaded wipes

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The purposes of this study are: (1) to determine whether proficiency analytical test (PAT) materials from the American Industrial Hygiene Association can be used to provide quality data for portable X-ray fluorescence analysis (XRF) of lead in dust wipe surface samples; (2) to provide data to determine whether the on-site analysis of field dust wipe samples by XRF and the laboratory method of inductively coupled plasma emission analysis (ICP) are comparable; and (3) to determine if differences exist between different wipe materials. Several wipes meet the ASTM E1792 performance requirements of lead background level less than 5 µg per wipe, be only one layer thick, yield recovery rates of 80–120% from spiked samples, remain damp throughout the sampling procedure, and do not contain aloe. The wipes used in this study were Pace Wipes, which are used for the PAT materials, and, for the field samples, Palintest Wipes, which were supplied by the instrument manufacturer, and Ghost Wipes, which are popular because they digest in hot, concentrated acid, so that chemical analysis is simplified. Twenty PAT wipe samples were obtained from four different proficiency test rounds. Surface wipe samples were taken at three different locations representing different industry types. All samples were analyzed using a portable XRF spectrometer and by ICP. Strong linear relationships were found for the analysis of wipe samples by ICP and by portable XRF. For the PAT samples, the results from the ICP and XRF analysis were not statistically equivalent, which indicates a bias in the ICP analysis. The bias was not excessive, since all ICP analyses fell within the acceptable range for the proficiency samples. The good correlation between the proficiency sample reference values and the XRF determinations is not surprising considering similar proficiency samples were used to calibrate the instrument response. Users of this portable XRF analyzer could enroll in the proficiency test program as part of their quality assurance program. For field samples, the relationship was strongest for Palintest wipes, and the values found for all three industries could be combined. However, the results from the ICP and XRF analysis were not statistically equivalent using the correction factor in the calculation algorithm as supplied with the instrument, and a new coefficient was derived. The mean relative error for the XRF analysis *versus* the ICP analysis was greater than 25%, such that the method falls within the realm of screening procedures. For Ghost Wipe samples, the precision was different for different industries, and the results could not be pooled. Differences between the two wipe materials may be related to the number of folds required for analysis.

Introduction

Lead usage has been dated back to before 2000 BC when lead was attained as a side effect of silver smelting. Today, the world mines more 2.7 million tons of lead per year.[1] Lead is used in many different applications because it has several desirable properties, such as high density, softness, low melting point, and resistance to corrosion.[2] Major uses include storage batteries, ammunition, nuclear and X-ray shielding devices, cable covering, ceramic glazes, noise control materials, bearings, brass and bronze, casting metals, solders, pipes, taps and bends. Lead was also a component of residential house paint prior to 1978.[3] The main routes of exposure to lead are through ingestion and inhalation.[4] The gastrointestinal tract absorbs approximately 5–10% of ingested lead,[5] whereas lead which is captured in the lungs during respiration is absorbed easily through the alveoli.[6] The respiratory tract can absorb around 40% of inhaled lead fume, but particle size and solubility determine the absorption of particulate lead.[5]

The nervous system, blood system, and kidneys are most impacted by lead exposure.[4] The major effect on the blood system is a lead induced anemia.[6] This anemia has been observed in adults at blood lead concentrations in the range of 50 to 80 µg dL^{-1}, but at lower levels in children.[7] Lead has been shown to cause detrimental effects on the myocardial function of humans at high concentrations of exposure,[8] and it also has been proven to cause small increases in systolic and diastolic blood pressure at blood lead concentration levels of 40 µg dL^{-1}.[7] Lead can have both acute and chronic effects on the kidneys,[6] including interstitial fibrosis, tubular atrophy, and dilation.[8] In adults, kidney damage has not been observed until blood lead concentration levels reach 100 µg dL^{-1}, but, again, lower levels have been shown to cause damage in children.[7] A typical symptom of lead exposure to the nervous system is peripheral neuropathy, which is characteristically expressed as a foot drop or wrist drop.[6] Slowed nerve conduction velocity has also been observed at blood lead concentration levels of 20 µg dL^{-1}.[7] High lead exposures in children can result in neurological effects and diminished mental capabilities.[6] A decrease in IQ in children has been displayed with blood lead concentration levels of 20 µg dL^{-1},[7] and brain damage at 80 µg dL^{-1}.[7] Lead has also been shown to produce infertility, germinal epithelium damage, oligospermia, decreased sperm motility, and prostatic hyperplasia.[9] Blood lead level concentrations in the range of 10 to 15 µg dL^{-1} have resulted in preterm birth and reduced birthweight.[7] The

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American Conference of Governmental Industrial Hygienist classifies lead as an A3 animal carcinogen, and it is considered a 2B animal carcinogen by the International Agency for Research on Cancer.[8] Lead is classified by the United States Environmental Protection Agency as a Group B2 carcinogen, which is a probable human carcinogen.[7] Renal adenocarcinoma has been generated in rats and mice through exposure to lead.[6]

The control of lead exposure in workers is primarily through the measurement of blood lead levels. However, air samples are used to determine the point at which a blood lead measurement program must be introduced. Using airborne lead levels to predict workers exposure ignores the contribution from ingestion. Ingestion can occur from hand contact with contaminated surfaces followed by transfer of the contamination from hand to mouth, either directly or *via* contact with food and smoking materials.

Lead compounds were commonly added to house paint prior to 1978. The Environmental Health Center has estimated that approximately two-thirds of the homes in the USA built before 1940 and half of the homes built between the years of 1940 and 1960 are contaminated with lead based paint.[10] The US Congress found that nearly 3 000 000 children under the age of 6 are affected by low level lead poisoning.[11] The Consumer Product Safety Commission discontinued the sale of lead based paint for residential usage in 1978.[3] Lead based paint was technically defined as paint, which contains 0.5 percent lead by weight, in 1992 by the Residential Lead-Based Paint Hazard Reduction Act.[12] Lead-based paint is a hazard when the paint is deteriorating, or when abrasion occurs on the surface. Wipe sampling can be used to determine the extent of the hazard. It can also be used in the clearance step as an aid in determining the completeness of remedial measures.

Occupational wipe samples

In both occupational and environmental hygiene it is important to characterize and control exposures from all routes. Wipe sampling is a valuable method for identifying hazardous conditions and determining the effectiveness of personal protective equipment, housekeeping, and decontamination programs.[13] The Occupational Safety and Health Administration (OSHA)'s Directive Number CPL 2-2.58, dealing with inspection and compliance procedures from lead exposure in construction states that wipe samples should be collected to prove that the contaminant is lead.[14] The same directive also states that the compliance safety and health officer should also collect wipe samples when there is a question about the contamination in lunchrooms, changing areas, and storage facilities.[14] The National Institute for Occupational Safety and Health (NIOSH) has developed method 9100, which is a method for analysis of lead in surface wipe samples.[15] This method states that the samples should be analyzed by flame or graphite furnace atomic absorption spectrometry (AAS), or inductively coupled plasma-emission spectroscopy (ICP). The OSHA has developed method ID-204, which is a qualitative X-ray fluorescence (XRF) analysis of workplace substances.[16] Although this method was developed for the analysis of air filters, wipe filters, and bulk material, wipe samples are not considered the best medium for this procedure.

Clearance wipe samples

One of the final steps of the lead abatement process is the clearance step in which visual inspections are made, dust samples are collected, soil samples are collected, and the paint is tested.[17] Wipe samples must be collected after the visual inspection because individuals with average eyesight cannot perceive particles with a diameters of less than or equal to 50 μm, and much of the lead dust which is generated during the abatement falls into this category.[17] Wipe samples are taken from positions around the area in which the abatement was completed, closely located areas of high traffic, or other locations determined to be of interest and samples should be taken from floors, window sills, and window troughs.[17] These clearance dust samples must be analyzed by laboratory methods such as AAS or ICP.[17] Portable XRF analyzers are not accepted methods for analyzing dust samples because they have not yet displayed the ability to accurately detect dust lead levels in the range of interest.[17]

The United States Department of Housing and Urban Development has set clearance levels of 40 μg ft^{-2} for bare and carpeted floors, 250 μg ft^{-2} for interior window sills, 800 μg ft^{-2} for window troughs, and 800 μg ft^{-2} for exterior concrete or other rough surfaces.[17] The OSHA recommends that a recommended level of 200 μg ft^{-2} be used for assessing the contamination of lead found in changing rooms, storage facilities, and lunchrooms.[14]

Off-site methods of analysis have disadvantages, mainly in the speed with which remedial measures can be undertaken. For example, off-site analysis of clearance samples in home lead abatement means longer waits before the occupants can return. In portable XRF analysis, high-energy X-rays expel electrons from shells (K and L) near the atomic nucleus. Other electrons then fill the gap in the orbital, with the emission of X-ray energy of wavelength characteristic for a specific element. The distinctive energy emissions are identified and quantified by the analyzer.[18,19] XRF analyzers are simple to use and require no chemicals. In practice, a folded wipe is placed under the X-ray window in various orientations, and the readings are averaged. A correction factor, to account for the loss of sensitivity with matrix depth, is then used to convert the averaged raw results to a total sampled mass. The correction provided by the manufacturer of the instrument that was used in this study is a multiplication factor of 3.3. The purpose of this study is to provide data to determine whether the on-site analysis of dust wipe surface samples by XRF and the laboratory method of ICP analysis are comparable, and to determine if differences exist between different wipe materials used for collecting wipe samples,[20] since several wipes meet the ASTM E1792 performance requirements of lead background level less than 5 μg per wipe, being only one layer thick, yielding recovery rates of 80–120% from spiked samples, remaining damp throughout the sampling procedure, and not containing aloe.[21] One way to examine the precision and accuracy of an analytical method is to use materials of a well-characterized composition. Proficiency test samples are available through the Environmental Lead Proficiency Analytical Testing (ELPAT) Program, which is managed by the American Industrial Hygiene Association (AIHA).[22] The samples are prepared by the Research Triangle Institute (NC, USA) by using actual paint chips, dusts, and soils. Their wipe samples are prepared by collecting dust from a number of sites and gravimetrically weighing them onto Pace Wipes. Once a round has been completed, it is possible to purchase the excess samples, and these come with the data compilation from their use in the proficiency scheme. For this study, 20 ELPAT wipe samples from previous test rounds were purchased, and were analyzed as quality assurance samples alongside the field samples. The mean ELPAT sample results varied from approximately 30–800 μg per filter (acceptable range 16–979 μg per filter, see Table 1).

Prior related studies

There have been very few studies on the use of wipes for lead in industrial situations or on the portable XRF analyzer for industrial hygiene samples. A study by Millson, Eller, and

Table 1 ELPAT samples published data

Sample ID	ELPAT mean/µg	ELPAT min./µg	ELPAT max/µg	Acceptable lower/µg	Acceptable upper/µg
Round 31 Wipe 1	82.50	70.00	98.10	58.20	106.70
Round 31 Wipe 2	416.30	343.60	798.50	298.40	534.20
Round 31 Wipe 3	799.50	667.20	901.40	619.70	979.30
Round 31 Wipe 4	172.50	139.30	199.50	127.80	217.30
Round 32 Wipe 1	58.60	45.90	73.20	37.10	80.00
Round 32 Wipe 2	130.20	106.00	151.00	95.40	165.00
Round 32 Wipe 3	239.00	197.30	279.00	176.80	301.20
Round 32 Wipe 4	29.80	23.20	40.00	16.10	43.40
Round 33 Wipe 1	555.80	455.90	630.10	415.40	696.30
Round 33 Wipe 2	49.30	37.50	63.40	29.60	69.00
Round 33 Wipe 3	117.20	95.00	135.50	83.20	151.30
Round 33 Wipe 4	334.50	297.00	383.60	250.80	418.10
Round 34 Wipe 1	117.00	96.10	133.10	86.60	147.40
Round 34 Wipe 2	408.70	337.50	484.00	288.20	529.10
Round 34 Wipe 3	41.30	31.00	49.80	25.60	56.90
Round 34 Wipe 4	201.60	171.00	230.50	150.50	252.60
Round 35 Wipe 1	88.00	72.50	102.00	62.70	113.20
Round 35 Wipe 2	561.90	483.00	621.00	438.60	685.20
Round 35 Wipe 3	256.70	214.00	303.70	179.70	338.80
Round 35 Wipe 4	41.50	32.20	52.00	26.40	56.60

Ashley evaluated wipe sampling materials for lead in surface dust, which concluded that the criteria to be used when choosing an acceptable substance for collecting wipe samples should include low background lead levels, high percent recovery of lead, high precision, and low variability in background lead concentrations from one wipe to another.[23] Another study by Chavalinitkul and Levins concluded "by proper selection of sampling wipe material and technique according to the nature of the test surface and accurately defining the sample area, wipe sampling can be significantly improved to provide a more reliable measure of the potential exposure to occupational and environmental surface contamination".[24] One study by Sterling, *et al.*, found that the "relative error of the concentration range of 25 to 14 200 µg of lead is −12% (95% CI, −18 to −5)," for the comparison of wipe samples analyzed by the XRF instrument and the analysis of the same samples by flame atomic absorption spectrophotometry.[25] It also found that the overall precision of the instrument is good and it is improved with the higher lead concentration levels, and found a correlation coefficient of 0.958 with a p-value of <0.001 and a slope of 1.08. A study that examined large numbers of samples from both industrial and residential sites[26] provided data for further evaluation. This study used the calculation algorithm with correction factor of 3.3 provided by the manufacturer and obtained a good correlation between XRF and ICP analysis, using Pace Wipes. However, the study may have been biased by the inclusion of many results below the estimated limit of quantitation. Recalculation after removal of these values also provides a good correlation, but requires a much higher correction factor. The OSHA is currently working on a draft method for the analysis of wipe samples.[27] The wipes used are Ghost Wipes, and a field study was carried out in several industrial situations, including lead-paint blasting and removal from freeway overpasses, lead–acid battery manufacture, metals reclamation, *etc.* The limit of quantitation is given as 22 µg. Both bias and precision were found to be below 5%, with good correlation. The factor used to correct the averaged raw XRF readings was 3.6, rather than 3.3. Palintest Wipes have not been tested in field studies.

Materials and methods

Sample collection

Palintest Wipes (Palintest, Ltd., UK) were supplied by the instrument manufacturer (NITON, Inc., MA, USA) and Ghost Wipes were obtained from Environmental Express, VA, USA. Both types of wipe materials meet the ASTM Standard specifications. Palintest wipes are recommended by the instrument manufacturer, and are 18.75 × 11.85 cm fully opened. Ghost wipes are smaller and made from a thicker material, but since the material digests easily in acid they are quite popular. They measure 14.25 × 10.5 cm fully opened. Other wipe materials, such as the Pace Wipes used to produce the ELPAT samples, are available, but were not used for field collection in this study. Pace Wipes are 15.4 × 13.5 cm fully opened. Card templates with a central 10 cm by 10 cm open area were used to delimit the sample area. Latex gloves were used to prevent cross contamination when collecting samples. Samples were placed in plastic bags with closures once collected.

X-ray fluorescence analyser

The NITON Model 700 Serial Number XL700-U2624NR1801, which contains a cadmium-109 source was used in this study. A metal dust wipe holder held the wipe for analysis. A test stage provided by NITON was used to place and position the dust wipe and metal dust wipe holder under the analyzer's X-ray beam. The two principal authors of this study had participated in the company-sponsored instrument use and safety training program.

Sample extraction

Extraction is the removal of specific analytes from a sample in solid form and transferring it into liquid form. Extraction must be performed on the wipe sample media for the sample to be injected into the ICP instrument. The current NIOSH method for the analysis of lead by ICP utilizes either hotplate or microwave digestion sample preparation techniques.[28] These methods of extraction involve the use of elevated temperatures and strong acids and the sample preparation step is in general the lengthiest step in the sample analysis. In order to shorten the sample analysis and remove the workers exposure to the concentrated acids and high temperatures, researchers have explored ultrasonic extraction method of samples for lead and have developed an American Society of Testing Materials method (ASTM E-1979-98) for the ultrasonic extraction of lead samples.[29,30] In this study, the samples and 10% (v/v) nitric acid were placed in 50 mL centrifuge tubes in a Branson 3510 ultrasonic bath for 30 min.

Sample size

For field sample collection, a sample size estimation was conducted using the data provided in the study conducted by Sterling, *et al.*[25] and the sample size equation published by Pagano and Guavreau.[31] The equation for sample size is provided as eqn. (1).

$$n = \left[\frac{(z_\alpha + z_\beta)(\sigma)}{\mu_1 - \mu_0}\right]^2 \tag{1}$$

where z_α = critical value for α, z_β = critical value for 1 − β, σ = standard deviation, μ_1 = relative error observed and μ_0 = relative error hypothesized.

The calculations for the determination for the sample size in study is:

$$n = \left[\frac{(1.96+0.84)(0.146)}{0.12-0}\right]^2 = 94.2 = 95 \tag{2}$$

Therefore a sample size of 95 samples was the goal for collection for both the Palintest Wipes and Ghost Wipes. This sample size is able to determine if the relative error of the XRF analysis when compared to the inductively coupled plasma analysis is greater than 12% with a 95% confidence and a power of 80%.

Wipe sample collection

Palintest Wipe samples were collected in accordance with the ASTM standard E1728[28] and the US Department of Housing and Urban Development (HUD) method for lead dust wipe sample collection.[17] Ghost Wipe samples were collected in accordance with the draft OSHA method.[27] The lead dust sample area was 10 cm by 10 cm as specified in the National Institute of Occupational Safety and Health lead surface wipe sample method, which yields an area of 0.010 m^2.[15] This area lies within the range of 0.0093 m^2 to 0.18 m^2 (0.1 to 2 ft^2) for sample areas given in the HUD guidelines.[17] Two blank wipes were sent in with each set of samples collected as per NIOSH Method 9100.[15] The samples were collected at three different industrial locations:

Battery plant. In the battery plant, the cases of the old batteries are removed and replaced. The grids of the lead plates are re-filled with lead oxide powder, and the lead contacts are cleaned before re-assembly. At the battery plant, samples were collected from an office and areas outside the building, as well as in the main facility.

Rebar plant. This plant uses large quantities of scrap metal, which can contain lead, in its process. The molten metal is poured into molds, which are later heated and extruded into reinforcing bar (rebar). The samples collected at the rebar plant were collected in the plant clean room, and locker room, as well as in the main facility.

Bullet plant. The bullet manufacturing plant uses lead in the production of bullets. In the process, scrap lead from sources such as tire weights is melted in a small furnace and pumped into a cast to form a billet. The billets are then put into a machine, which draws the lead into a wire that meets the diameter of the bullet to be made. The wire is then run through another machine to cut the wire to the desired length. Samples were collected around the furnace, in the lead storage area, and in the test firing range.

Procedure for X-ray fluorescence analysis of wipe samples

Calibration. The XRF analyzer's calibration was checked with thin film standards from Micromatter Company (Deer Harbor, WA, USA). These standards are Nucleopore polycarbonate membranes coated with specified metals and designed for use in the calibration of XRF equipment. The thin film standard identified by serial number 13099 has a 23-mm diameter and has a lead concentration of 58.7 μg cm^{-2} with a relative error of ± 5%. The thin film standard identified by serial number 13100 has a 32-mm diameter and a lead concentration of 59.4 μg cm^{-2} with a relative error of ± 5%. A further, high-level check on the calibration was obtained by using the NITON Dust Wipe check system 0012-17A, which has a concentration range of 480–620 μg.

Procedure. The wipe medium was placed at the corner of the template, and pressing down firmly, wiped from side to side with as many S-like motions as needed to cover the area. The wipe was folded in half with the contaminated side facing inward, and the S wiping motion was repeated going from top to bottom. The Palintest Wipes were folded in half three more times (total of five folds) to produce a pad about 3.0 × 2.4 × 0.6 cm. In the OSHA Draft Method,[27] the Ghost Wipes, which are smaller and thicker, were only folded two more times (total of four folds) to produce a pad about 3.5 × 2.6 × 0.5 cm. Ghost Wipes given an extra fold were found to be too thick to fit into the holder, and thus they were only folded four times. The procedure for folding the ELPAT samples involves a slightly different methodology, since to produce the ELPAT samples the leaded dust sample is placed in the center of the wipe before folding for transportation. This does not mimic the normal spread of dust from sampling, and so ELPAT wipes, therefore, were carefully opened, and the dust deposit spread more evenly over the wipe before re-folding. Pace Wipes folded five times produced a pad about 3.2 × 1.9 × 0.6 cm. All folded wipes were placed in a clean plastic bag, and the bag was placed in a metal dust wipe holder. The holder was placed on the number one position of the test stand and the first measurement was taken. The holder was then placed in the number two position of the test stand and the second measurement was taken. The holder was then rotated 180° (without turning the holder over) and the third measurement taken in the number one position and the fourth measurement taken in the number two position. The mass of lead on the wipe sample as calculated automatically by the instrument, using eqn. 3, and also the individual readings were recorded. All measurements involved counts accumulated for 60 nominal seconds.

$$M_{\mu g} = (\text{Reading}_{\#1} + \text{Reading}_{\#2} + \text{Reading}_{\#3} + \text{Reading}_{\#4}) * 3.30 \tag{3}$$

ICP analysis of wipe samples

Analysis was carried out at DHL Laboratory (Birmingham, AL, USA) using a PerkinElmer Plasma 400 ICP, set to a wavelength of 220.4 nm. NIOSH method 7300 was followed for the analysis of extracted samples for lead by ICP.[28] Each centrifuge tube from the extraction step was uncapped and the sample was made to the 50 mL mark with distilled, deionized water. The tubes were then capped, shaken for five to ten seconds, and allowed to settle. The ICP was calibrated according to the manufacturers recommendations. Standards were analyzed each day of analysis in the range of 0.8 μg mL^{-1} to 20 μg mL^{-1} with correlation coefficients greater than 0.999. A check standard was run every ten samples, and recoveries were checked with at least two spiked media blanks per ten samples. During the period of this study the laboratory, while not accredited by the American Industrial Hygiene Association, participated in their on-going Proficiency Analytical Testing programs for metals and was rated proficient.

Statistical analysis

Analysis of variance (ANOVA). ANOVA tests were conducted for each wipe media to determine if the samples collected at each site could be combined. The null hypothesis for the data was that the variance values reported from each site were equal. The alternate hypothesis was that the variance values reported from each site were not equal.

Linear regression. Linear regression was conducted separately for each dust wipe media comparing the analysis by XRF and analysis by ICP. If the ANOVA test resulted in accepting the null hypothesis, then the data for the samples collected for each site were combined and linear regression was conducted for all of the data collected at each site combined.

Paired *t*-test. Two-sided test of hypotheses were conducted for each type of wipe sample media for each plant the wipe media were collected at, comparing the analysis by XRF and analysis by ICP. If the ANOVA tests concluded to accept the null hypothesis, all of the samples were combined and a paired *t*-test was conducted between the ICP analysis and XRF analysis.

Results and discussion

The ICP results of the ELPAT sample analysis all fell within the acceptable range for those samples. The mean relative error between the ELPAT published means (Table 1) and the NITON results was calculated to be 19%. The mean relative error between the in-house ICP results and NITON results was calculated to be 26.8%. Linear regression was conducted between the ELPAT means, and the in-house ICP analysis results. The results of this analysis yielded a slope of 1.17 with a correlation coefficient of 0.996. A scatter plot of the ELPAT means *versus* the ICP results is displayed as Fig. 1. Linear regression was conducted between the ELPAT sample means and the XRF analysis results using the NITON algorithm yielding a slope of 0.914 with a correlation coefficient of 0.969. A scatter plot of the ELPAT means *versus* the XRF results is displayed as Fig. 2. Linear regression was then conducted between the ICP analysis results and the XRF analysis results using the NITON algorithm yielding a slope of 0.784 and a correlation coefficient of 0.973. A scatter plot of the ICP results *versus* the XRF results is displayed as Fig. 3.

Paired *t*-tests were conducted between the ELPAT means and in-house ICP results (-4.07, $p = 0.0007$), ELPAT means and NITON algorithm results (0.95, $p = 0.354$), and in-house ICP results and NITON algorithm results (3.12, $p = 0.0056$).

While in-house ICP results were not statistically equal to either the ELPAT means or the NITON results, the ELPAT means and the NITON algorithm results are statistically equal.

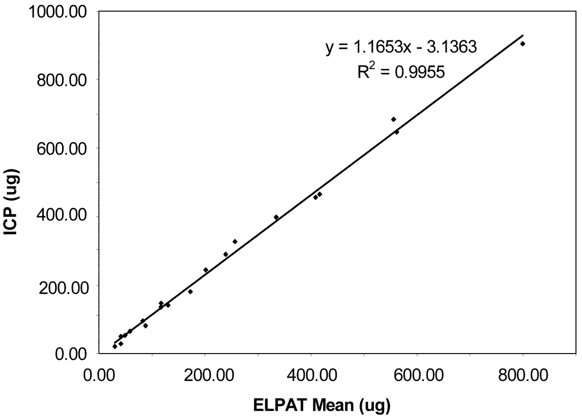

Fig. 1 ELPAT means *versus* ICP results.

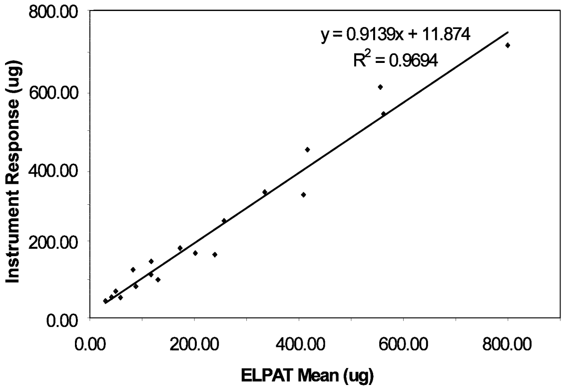

Fig. 2 ELPAT means *versus* XRF results.

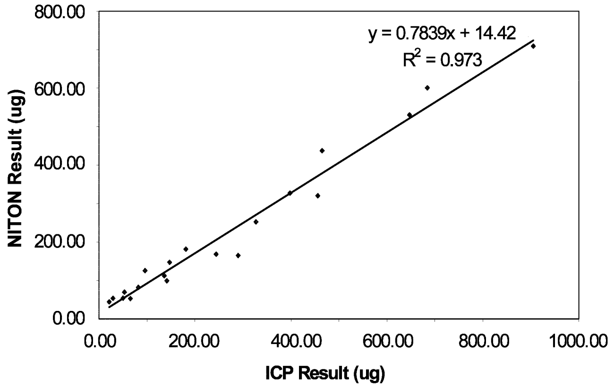

Fig. 3 ICP results *versus* XRF results for ELPAT samples.

There are several possible reasons for these results. One is that the observed bias between the in-house ICP results and the ELPAT published means results from a bias within the in-house analysis, although this could not be confirmed by a review of the in-house quality control data. Another possible cause is that sonic extraction actually recovers more lead from the wipes than does the hot, concentrated acid digestion used by the majority of ELPAT participants. Despite the bias, the results are still acceptable since the ICP results all fell within the ranges considered acceptable for the ELPAT program. Although AIHA does not recommend that ELPAT samples be used for calibration purposes, to determine the effect of this bias on the results from field samples, the ICP results from the field samples were corrected using the equation for the relationship between the ICP results for the ELPAT samples and ELPAT published means. Paired *t*-tests, linear regression, and relative error were performed on the field data using the corrected ICP results. In general, relative errors were decreased, and *t*-values and *p*-values came closer to the acceptable range, but no test result was overturned, and the correction does not have a significant effect on the outcome of the study. If the ELPAT published means are taken as the "reference value", it is encouraging to see that the relationship with the NITON algorithm results is not only strongly linear, but also statistically significant. However, this should not be so surprising, when it is considered that the NITON algorithm is based on a prior analysis of similar ELPAT samples.[32]

ANOVA

An ANOVA statistical test was conducted between the samples collected at all three plants to determine if they could be combined. For the Ghost Wipe samples, the ANOVA test for the NITON algorithm results for all three plants gave a F-statistic of 6.8, which is greater than the $F_{0.95}(2,92)$-statistic of 3.95. Thus the variance of the samples was not equal, and the data cannot be combined for all three sites. For the Palintest Wipe samples, the ANOVA test for the NITON algorithm results revealed a F-statistic of 1.85, which is less than the $F_{0.95}(2,92)$-statistic of 3.95. This indicates that the values from all three sites can be combined.

Relative error

For the Bullet plant, the mean relative error for the Ghost Wipe NITON results was calculated to be 60.3%, while the mean relative error for the Palintest Wipe results was calculated to be 43%. For the Rebar plant, the mean relative error for the Ghost Wipe NITON results was calculated to be 37.8%, while the mean relative error for the Palintest Wipe results was calculated to be 27.8%. For the Battery plant, the mean relative error for the Ghost Wipe NITON results was calculated to be 76%, and the mean relative error for the Palintest Wipe results was calculated to be 35.6%. For the combined Palintest results, the mean relative error was calculated to be 36%.

Linear regression

Bullet plant. Eighty-five samples were collected at the bullet plant. Forty-three of these samples were collected using the Ghost Wipe media, and forty-two of the samples were collected using the Palintest Wipe media. A statistical test for normality was performed on the data and it was concluded that the data was log normally distributed. For the Ghost Wipes, linear regression between the natural logs of the ICP results and the XRF results gave a correlation coefficient of 0.9145 ($p < 0.0001$), and a slope of 0.729 (standard error 0.035). The scatter plot is given as Fig. 4.

The linear regression that was performed on the Palintest Wipes yielded a correlation coefficient of 0.902 ($p < 0.0001$), and a slope of 0.774 (standard error 0.04). The scatter plot is displayed as Fig. 5.

Battery plant. Forty-five samples were collected at the battery plant. Twenty-two of these samples were collected using the Ghost Wipe media, and twenty-three of the samples were collected using the Palintest Wipe media. The sample results for the battery plant for the Ghost Wipe media yielded one sample, which was below the limit of detection for the ICP. This non-detect was treated by using the Winsorization treatment method. Again, a statistical test for normality showed the data to be log normally distributed. Linear regression between the natural logs of the ICP results and the XRF results gave a correlation coefficient of 0.812 ($p < 0.0001$), and a slope of 0.844 (standard error 0.104). A scatter plot is displayed as Fig. 6.

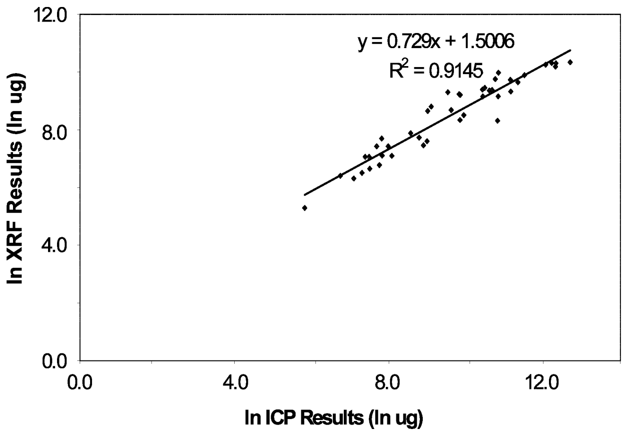

Fig. 4 Bullet plant Ghost Wipe natural log of ICP *versus* natural log of XRF.

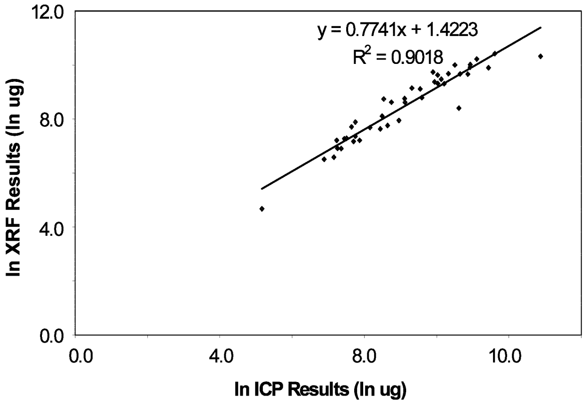

Fig. 5 Bullet plant Palintest Wipe natural log ICP *versus* natural log XRF.

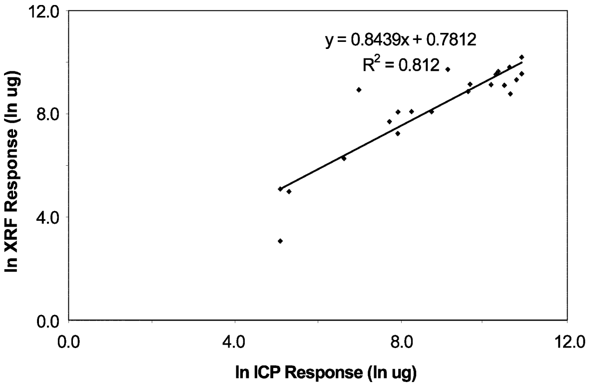

Fig. 6 Battery plant Ghost Wipe natural log ICP results *versus* natural log XRF results.

For the Palintest data linear regression between the natural logs of the ICP results and the XRF results gave a correlation coefficient of 0.809 ($p < 0.0001$), and a slope of 0.826 (standard error 0.088). A scatter plot of the ICP results *versus* the XRF results is displayed as Fig. 7.

Rebar plant. Sixty samples were collected at the rebar plant. Thirty of these samples were collected using the Ghost Wipe media, and thirty of the samples were collected using the Palintest Wipe media. The sample results for the rebar plant for the Ghost Wipe media yielded five samples, which were

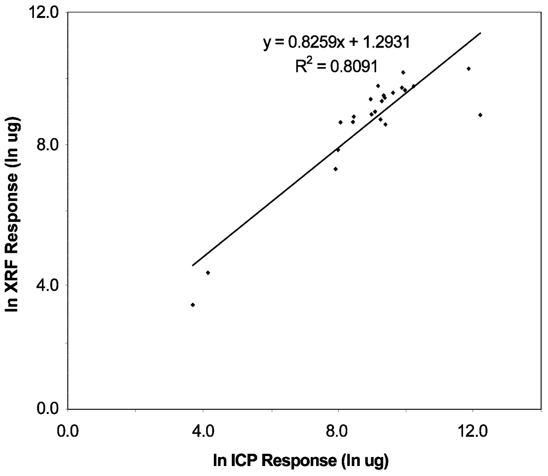

Fig. 7 Battery plant Palintest Wipe natural log ICP results *versus* natural log XRF results.

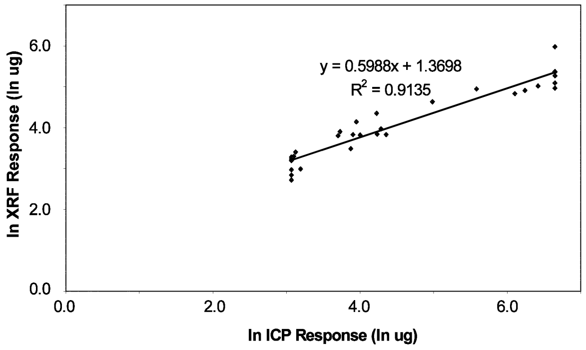

Fig. 8 Rebar plant Ghost Wipe natural log ICP results *versus* natural log XRF results.

below the limit of detection for the ICP, and the sample results for the Palintest Wipe yielded five samples, which were below the limit of detection for the ICP. These non-detect values were treated by using the Winsorization treatment method.

Again, the Ghost Wipe data was found to be log normally distributed and linear regression between the natural logs of the ICP results and the XRF results gave a correlation coefficient of 0.914 ($p < 0.0001$), and a slope of 0.599 (standard error 0.035). A scatter plot is displayed as Fig. 8.

For the Palintest results, linear regression between the natural logs of the ICP results and the XRF results gave a correlation coefficient of 0.937 ($p < 0.0001$) and a slope of 0.816 (standard error 0.051). A scatter plot is displayed as Fig. 9.

Combined Palintest Wipe samples. The ANOVA statistical test indicated that the NITON algorithm values from all three sites can be combined. The combined data set was also found to be log normally distributed. Linear regression between the natural logs of the ICP results and the XRF results was conducted and produced a correlation coefficient of 0.953 ($p < 0.0001$) with a slope of 0.89 (standard error 0.021). The scatter plot is displayed as Fig. 10.

Paired *t*-test

Bullet plant. Paired *t*-tests were conducted between the ICP results and NITON result, for the Ghost Wipes and for the Palintest Wipes. The results of the paired *t*-tests were 3.81 (p-value = 0.0005) for the Ghost wipes and 2.30 (p-value = 0.0265) for the Palintest wipes. For both tests, the conclusion is to reject the null hypothesis of the mean results being equal.

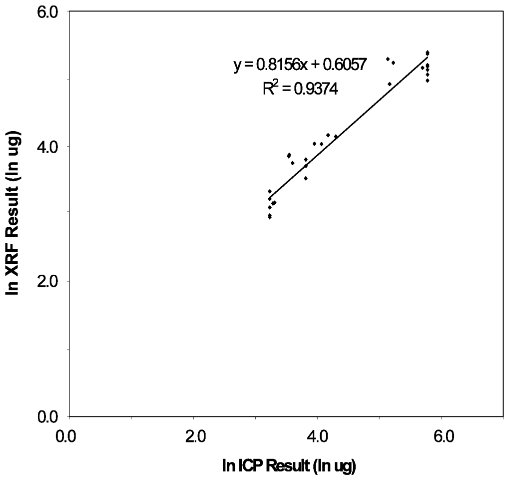

Fig. 9 Rebar plant Palintest Wipe natural log ICP results *versus* natural log XRF results.

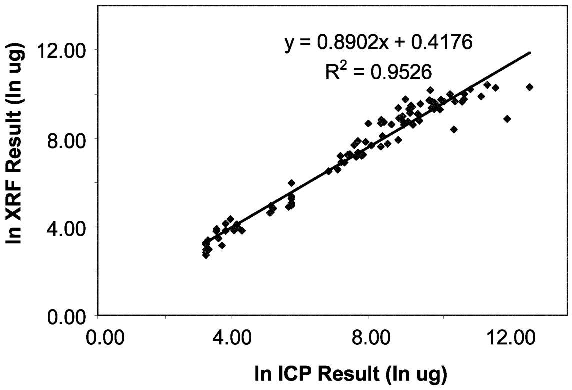

Fig. 10 Palintest Wipe combined data natural log ICP results *versus* natural log XRF results.

Rebar plant. Paired *t*-tests were conducted between the ICP results and NITON result, for the Ghost Wipes and for the Palintest Wipes. The results of the paired *t*-tests were 3.64 (p-value = 0.0010) for the Ghost Wipes and 3.07 (p-value = 0.0046) for the Palintest Wipes. For both tests, the conclusion is to reject the null hypothesis of the mean results being equal.

Battery plant. Paired *t*-tests were conducted between the ICP results and NITON result, for the Ghost Wipes and for the Palintest Wipes. The results of the paired *t*-tests were 3.61 (p-value = 0.0016) for the Ghost Wipes and 1.42 (p-value = 0.1683) for the Palintest Wipes. For both tests, the conclusion is to reject the null hypothesis of the mean results being equal.

Palintest Wipe combined data. Since the ANOVA analysis indicated that the Palintest Wipe sample collected at each plant can be combined, a paired *t*-test was conducted between the ICP results and NITON results, with a *t*-value of 2.68 and a p-value of 0.0087. Again, the conclusion is to reject the null hypothesis of the mean results being equal.

ICP correction. Since the lead was extracted by using ultrasonic means instead of hot plate extraction and the ultrasonic extraction method appeared to recover more lead than the hot plate extraction method and the XRF algorithms are related to the traditional methods of extraction, one possible explanation for why the XRF data is below the ICP result could be related to the ICP extraction method. Although AIHA does not recommend that ELPAT samples to be used for calibration purposes, the ICP results were corrected using the equation for the relationship found between the ICP result and ELPAT mean. Paired *t*-tests, linear regression, and relative error were performed on the data using the corrected ICP results. The results of these statistical tests are displayed in Table 2.

In general, the ICP correction did not greatly affect the results of the statistical analysis.

Palintest combined data

For the Palintest Wipe samples, a relative error 36.4% was yielded between the ICP result and NITON XRF result, which was reduced to 33% with the ICP correction. The linear regression that was conducted between the natural logs of the two sample methods produced a correlation coefficient of 0.953, which indicates that a there is a linear relationship between the ICP result and the NITON XRF result, and it also yielded a slope of 0.890, which indicates that the NITON algorithm could be producing results that are below the actual value. The conclusion of the paired *t*-test, however, was to reject the null hypothesis of the mean ICP result being

Table 2 ICP corrected data

		Paired *t*-test			Linear regression	
Plant site	Wipe media	*t*-value	*p*-value	RE	r^2	Slope
Bullet plant	Ghost	3.73	0.0006	54%	0.914	0.729
Bullet plant	Palintest	2.16	0.0367	37%	0.901	0.773
Rebar plant	Ghost	3.53	0.0014	36%	0.91	0.619
Rebar plant	Palintest	2.20	0.0359	27%	0.898	0.838
Battery plant	Ghost	3.33	0.0032	75%	0.742	0.803
Battery plant	Palintest	1.24	0.2275	41%	0.806	0.831
Combined	Palintest	2.47	0.0154	33%	0.935	0.899

Table 3 Statistical test results with new algorithm

	Paired *t*-test		Linear regression		
Plant	*t*-value	*p*-value	Slope	S.E.	Corr. coeff.
Combined Palintest	1.85	0.0667	0.89	0.021	0.953
Bullet plant	1.74	0.0898	0.772	0.04	0.901
Rebar plant	−1.58	0.1259	0.805	0.051	0.905
Battery plant	0.73	0.4755	0.826	0.088	0.809

equal to the mean NITON XRF result. A new algorithm was generated, by replacing the coefficient of 3.3 in eqn. (3) with a coefficient of 5.4. The results of statistical tests using the new algorithm are given in Table 3.

There was little change in the linear regression analysis, but all of the paired *t*-tests for the individual plant samples concluded to accept the null hypothesis of the XRF method and ICP method being statistically equal.

Conclusions

Strong linear relationships were found between the natural logarithms of the XRF results and the ICP results for both types of wipe, but only the data from the three plants from the Palintest Wipes could be combined. Differences in the slopes from the three different industries may be attributable to different particle sizes and compositional differences for the dust matrices containing the lead in the different plants, or to the concentration ranges being different. Using the NITON algorithm (3.3 correction factor) for calculation of the total mass of lead by XRF underestimated the mass of lead compared to the ICP analysis. Even with a correction to the ICP results using the relationship based on the analysis of proficiency test samples the difference was still significant. A new algorithm, using a correction factor of 5.4, was found to be a better fit for the Palintest Wipe data. The NITON algorithm is based on calibration using proficiency test samples on Pace Wipe samples and this may be the reason for the difference. It would be interesting to compare the OSHA correction (3.6) found for the Ghost Wipe data from their study with the data found in this study, but, unfortunately, the Ghost Wipe data in this study could not be combined. The difference in the multiplier found for the Palintest Wipes in this study and that found for the Ghost Wipes in the OSHA study may be due to the difference in the number of folds, and, therefore, the difference in the distribution of lead through the sample, or it may be due to the different matrix material. More research is required to confirm and explain this difference. In this study, the Palintest Wipes yielded slopes closer to 1, correlation coefficients closer to 1, *t*-values closer to the acceptable range, and lower relative errors than did the Ghost Wipes.

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