



Evaluation of two portable lead-monitoring methods at mining sites

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Abstract

Two methods for measuring airborne lead using field-portable instruments have been developed by the National Institute for Occupational Safety and Health (NIOSH): Method 7702 uses X-ray fluorescence (XRF), and Method 7701 employs ultrasonic extraction (UE) followed by anodic stripping voltammetry (ASV). The two portable methods were evaluated at mining sites. Area air samples were collected throughout two mills where ore from nearby mines was processed; the primary constituent of the ore was lead sulfide (galena). The air samples were collected on 37 mm mixed cellulose ester membrane filters housed within plastic filter cassettes. At the end of the work shift, the cassettes were collected and taken to a room off-site for analysis by the two portable methods. The filter samples were first analyzed by XRF and then by UE/ASV. Calibration was verified on both instruments according to standard procedures. The samples were then sent for confirmatory analysis via flame atomic absorption spectrometry (FAAS) according to NIOSH Method 7082. Pairwise comparisons between the methods using the paired *t*-test showed no statistically significant differences between ASV and FAAS ($P > 0.05$); however, the comparison between XRF and FAAS was statistically significant ($P < 0.05$). The elevated lead concentrations reported by XRF relative to FAAS were likely the result of the ability of XRF to report total lead, including lead silicates. This form of lead is not liberated in the digestion process prior to FAAS analysis, and is therefore not detected by this method. Despite this discrepancy, lead concentrations measured by both portable technologies were found to be highly correlated with the laboratory

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method ($R^2 > 0.96$), suggesting that they are suitable as screening methods for airborne lead at mining sites.

Published by Elsevier B.V.

Keywords: Lead; Anodic stripping voltammetry; X-ray fluorescence; Portable analysis; Ultrasonic extraction

1. Introduction

Numerous adverse health effects are associated with overexposure to airborne metals [1]. Many problems do not appear until weeks, months, or even years after exposure has ended. Field-portable instruments could be useful tools in protecting workers from excessive airborne metal exposures that could reduce the quality of life in their retirement years. At the present time, the most commonly used methods for assessing workplace airborne metal exposures involve collecting air samples on filters and sending them to a fixed-site laboratory where a variety of analytical methods are used. Although reference fixed-site laboratory methods are accurate and have low detection limits, the length of time from sample collection to receipt of measurement data is often unacceptably long, because workplace risk management decisions depend on the exposure assessment results. Therefore, cost-effective on-site monitoring techniques for measuring metal concentrations with near real-time (end of shift) speed could be extremely useful.

The National Institute for Occupational Safety and Health (NIOSH) has developed two quantitative field-portable methods to measure airborne lead: NIOSH Method 7702, which uses X-ray fluorescence (XRF) [2], and NIOSH Method 7701 [3], which uses ultrasonic extraction (UE) and anodic stripping voltammetry (ASV). These methods have been used successfully in the construction industry and at hazardous waste sites [4–7]. Specifically, UE/ASV has been shown to be a viable technique for the analysis of lead in workplace samples [4,8,9], and portable XRF is capable of identification, characterization, and measurement of trace element concentrations in surface, soil, and air samples [10,11]. However, these techniques have not been widely used to evaluate workplace exposures, particularly at mining sites, where matrix effects are potentially different.

In the present study, two on-site methods involving the use of a field-portable XRF and UE followed by ASV for the determination of lead in workplace air filter samples were investigated. The purpose was to evaluate the two portable methods at mining sites, where the metallurgy of lead compounds may be different from those found at construction sites.

2. Sampling and analytical methods

Sixty-eight area air samples were collected throughout two mills where mined ore was processed. The primary constituent of the ore was galena (lead sulfide). After the ore is mined, it is crushed in a rod or ball mill. The finely crushed material is then mixed with various chemicals [1,12], and the sulfides are separated by flotation. The lead concentrates are then subjected to a thickening process, filtered, and dried. Finally the treated concentrates are shipped off-site for refining. To obtain a wide concentration range of lead on the filters,

area air samples were collected in the mill work area over two consecutive days at each step in the above process. To obtain lower loadings, area air samples were also collected in the lunchroom, computer room, and in an office area.

Sample collection was carried out according to an established NIOSH Method [13]. Briefly, the method involved drawing air through mixed cellulose ester (MCE) membrane filters (37 mm diameter, 0.8 μm pore size; SKC, Eighty-Four, PA) at a flow rate of 2 (± 0.1) l/min using GilAir 5 personal sampling pumps (Sensidyne, Clearwater, FL). Sample collection times ranged from <30 to 454 min. All pumps were calibrated in the field before and after sampling, using a BIOS DryCal DC-Lite primary flow meter (BIOS International Corp., Pompton Plains, NJ). At the end of the work shift, the filter cassettes were collected and taken to a room off-site for analysis using the two field-portable methods. Each sample was then packaged and sent to be analyzed by confirmatory laboratory-based atomic absorption spectrometric methods. The overall order of analysis was as follows.

2.1. NIOSH Method 7702

The collected filters were carefully removed from the filter cassettes using Teflon-coated forceps (Cole-Parmer, Vernon Hills, IL) and mounted between Mylar[®] sheets (Dupont, Wilmington, DE) in specially designed cardboard sample holders (NITON, Bedford, MA). The sample holders kept the filters clean during handling and analysis, and prevented curling. Each sample holder was used only once to eliminate the possibility of cross-contamination between samples. The filters were analyzed by portable XRF using a Model XL 701 Thin Sample Analyzer (NITON). Using lead standards of certified concentrations (National Institute of Standards and Technology (NIST), Standard Reference Material (SRM), 3087a, Metals on Filter Media, Gaithersburg, MD), instrument calibration was verified to be within $\pm 5\%$ on instrument start-up, after every 10th sample, and at the end of the sampling day.

2.2. NIOSH Method 7701

The UE/ASV method was carried out following the portable XRF analysis. The filters were removed from the sample holders and placed in 30 ml Oak Ridge sealable centrifuge tubes (Nalge Co., Rochester, NY). A total of 10 ml of 10% trace-metal-grade nitric acid (Fisher, Pittsburgh, PA) was added to each tube with a mechanical pipet (Eppendorf, Hamburg, Germany). Any visible dust deposits on the Mylar sheets were washed into the tube using part of the 10 ml nitric acid solution. The centrifuge tubes were placed in an ultrasonic bath (Crest Model 575T, Trenton, NJ), and the level of the water in the bath was adjusted to a height of 2.5 cm above the liquid in the centrifuge tubes. The samples were sonicated for 30 min. After the samples cooled to room temperature, 15 ml of deionized water (Barnstead Nanopure system, Thermolyne, Dubuque, IA) was added to each sample, bringing the total volume of each sample to 25 ml.

While the sonicated samples were settling, electrolyte tablets (SP-B, Palintest, Gateshead, UK) were placed in 5 ml polypropylene sample vials (Palintest). A 5 ml aliquot of each sample was then pipetted into the sample vials, and the electrolyte tablets were crushed with a clean plastic stirring rod. The samples were analyzed for lead with a Palintest 5000 Scanning Analyzer (SA) using disposable electrodes (SE-1, Palintest).

Quality control (QC) samples were analyzed to evaluate the performance of the Palintest 5000 SA instrument. Some of the QC samples analyzed were NIST SRM Buffalo River sediments (SRM 2704, 0.016% Pb by mass; SRM 2582, 0.0209% Pb by mass). Other QC materials were also analyzed; these consisted of samples obtained from the Environmental Lead Proficiency Analytical Testing (ELPAT) program, Round 007 (Paint 1, 0.1135% Pb; Paint 3, 0.2729% Pb; Paint 4, 1.7189% Pb; Soil 1, 0.09594% Pb) [14]. The QC samples were weighed in the field on a portable balance to ± 0.002 g (Acculab Pocket Pro C/50, Newtown, PA) and subjected to the UE/ASV procedure described earlier.

2.3. NIOSH Method 7082 without digestion

The centrifuge tubes were sealed and sent to a laboratory accredited under the Environmental Protection Agency (EPA) National Lead Laboratory Accreditation Program (NL-LAP) [15] for confirmatory analysis. A 10 ml aliquot was removed from each tube and analyzed for lead using a flame atomic absorption spectrometer (FAAS) (Varian 220-FS, Palo Alto, CA).

2.4. NIOSH Method 7082 with digestion

The remaining 15 ml of solution, together with the filter, were digested with concentrated instrumental grade nitric acid (EM Science, Gibbstown, NJ) according to NIOSH Method 7082, which was modified for microwave digestion (MDS 2100, CEM, Matthews, NC). All digested samples were analyzed for lead using a Varian 220-FS FAAS.

3. Statistical analysis

Statistical analyses were performed using Statistical Analysis System 6.12 and StatView 5.01 (SAS Institute, Inc., Cary, NC). The best-fit line through the data and the correlation coefficient were determined using least squares linear regression. Statistical tests were conducted to determine if the slope of the best-fit line was significantly different from unity at the $\alpha = 0.05$ significance level [16]. The log-transformed data were used when calculating bias, relative standard deviation (R.S.D.), and accuracy.

4. Results and discussion

The overall objective of this study was to rigorously compare the data obtained using the two field-portable methods to analytical results from traditional fixed-site laboratory methods. The FAAS acid-digested method of analysis was determined to be the reference method, so the other three methods (described in Sections 2.1–2.3) were compared to it. Statistical tests were conducted to determine if the methods performed equivalently. The correlation coefficients (R^2 -values) and the equation for the best-fit line are shown for each method comparison (Figs. 1–3). The purpose for displaying the unity line ($y = x$) is to show how well the slope of the best-fit line compares to a slope of one. Ideally, if both methods were free from any bias or error, the best-fit line should have a slope of one and fall on line $y = x$.

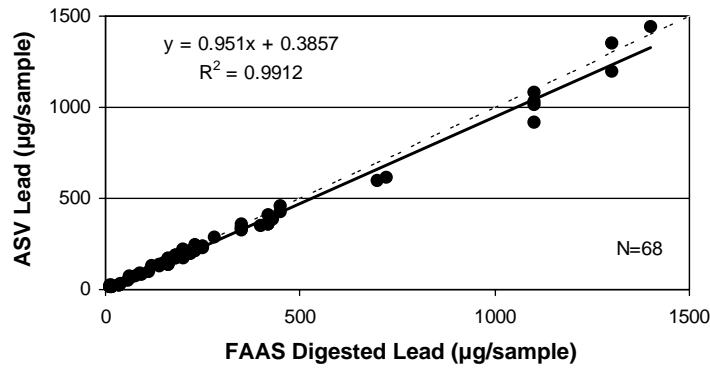


Fig. 1. Results from UE/ASV compared to FAAS acid-digested (reference method). The solid line through the data indicates the line of best fit. The dashed line represents $y = x$, or unity slope and zero intercept.

Both the XRF and ASV methods reported results greater than 10 µg Pb per sample. Samples with values below the ASV and XRF reporting limit were excluded from data analysis. The actual method detection limits of both the ASV and XRF instruments are below 10 µg per sample [4,6,7], but the instrumental software does not show results below these values.

Results from the ASV method compared to the reference method (FAAS acid-digested) are shown in Fig. 1. The slope of the line is slightly less than one, the y-intercept is very near zero, and the correlation coefficient is close to unity. These data show the reported ASV lead concentrations to be very strongly correlated with concentrations obtained from traditional laboratory methods. The performance of the Palintest 5000 SA instrument was evaluated using NIST SRMs containing known concentrations of lead, and all QC samples gave quantitative lead recoveries, i.e. $100 \pm 20\%$ [17].

Fig. 2 shows the results from the comparison between the portable XRF method and the reference method. The best-fit line through the data shows a correlation coefficient close to

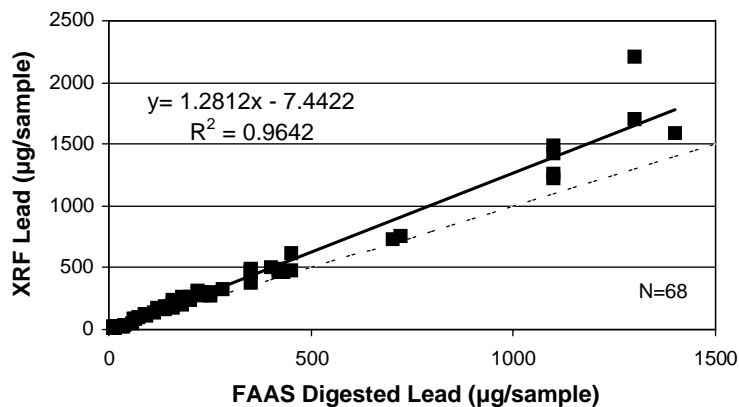


Fig. 2. Results from portable XRF compared to FAAS acid-digested (reference method). The solid line through the data indicates the line of best fit. The dashed line represents $y = x$, or unity slope and zero intercept.

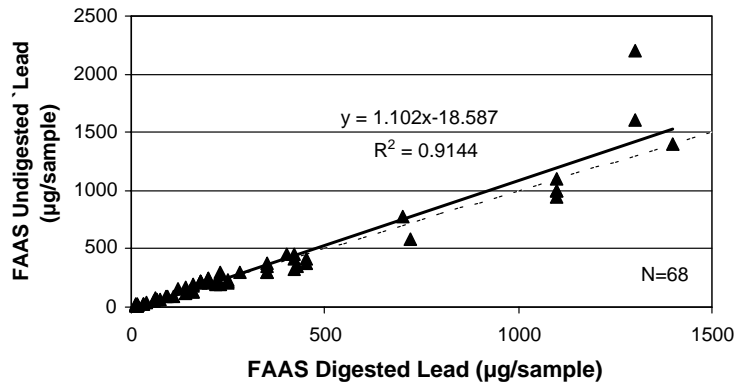


Fig. 3. Results from FAAS-undigested compared to FAAS acid-digested (reference method). The solid line through the data indicates the line of best fit. The dashed line represents $y = x$, or unity slope and zero intercept.

unity and a slope of 1.28. This means the reported XRF concentrations were positively biased compared to the reported reference method. A possible explanation is the XRF instrument has the ability to measure all forms of lead, including lead silicates. The reference method used in this study cannot measure all lead that is bound to silicate minerals and is therefore not extracted during the digestion procedure and subsequently analyzed. Measuring lead silicates would necessitate a digestion method using hydrofluoric acid [18]. The calibration of the NITON 701 XRF was evaluated using a standard containing a total of 101 µg lead, which was produced by techniques consistent with NIST SRM 3087a (i.e. lead acetate in solution was spiked onto filter material).

The two laboratory methods (i.e. extracted versus digested) were compared to determine how well they agreed (Fig. 3). The slope of the line is slightly greater than one (1.102), and the correlation coefficient is close to unity (0.914). These data suggest that the two laboratory-based methods are highly correlated with one another. The implication is that digestion recovers no additional significant amount of lead from the sample that was previously subjected to ultrasonic extraction. This observation is in keeping with previously reported results [4,8].

Pairwise comparisons between the three tested methods and the reference method were done using a paired t -test. No statistically significant differences were seen between the UE/ASV and FAAS-undigested method when compared to the reference method ($P > 0.05$). The comparison between the XRF and the reference method was statistically significantly different ($P < 0.05$). Precision, bias, and accuracy of the methods were also determined and compared. Since the actual bias of each method was unknown, the FAAS acid-digested method was treated as the reference method and was assumed to have no bias. The bias for the other methods was determined by comparing results from the method under consideration with the reference method. Since there were no repeated measurements of the same sample, or samples with the same concentration for a given method, R.S.D.'s could not be directly estimated with the data from a single method. However, using the pairwise data from all methods, the variability from one method relative to the other was separated. Note that the R.S.D. under the original scale is approximately equal to the standard deviation

Table 1
Bias, precision (R.S.D.), and accuracy estimates for each lead measurement method studied ($N = 68$)

Method	Bias	R.S.D.	Accuracy	Confidence interval	
				5%	9%
UE/ASV	-0.002	0.080	0.157	0.138	0.183
XRF	0.265	0.133	0.479	0.442	0.526
FAAS-undigested	0.023	0.122	0.244	0.215	0.285
FAAS-digested	-	0.140	0.274	0.241	0.320

of the log-transformed data. If X and Y are the results from the same sample but from two different methods, then $\ln(X/Y) = \ln(X) - \ln(Y)$ has a standard deviation equal to $\sqrt{[\text{R.S.D.}(X)]^2 + [\text{R.S.D.}(Y)]^2}$. R.S.D. estimates for the four methods were obtained by solving these R.S.D. equations. The accuracy estimate for each method was determined using the estimated bias and R.S.D. Estimates of bias, R.S.D., and accuracy are shown in Table 1. NIOSH accuracy criteria require that a method must give a result that is within $\pm 25\%$ of the true concentration value at least 95% of the time [15]. The UE/ASV method is the only method that meets the NIOSH accuracy criterion ($A < 25\%$). Very little bias is shown between the ASV method and the reference method, and the R.S.D. is $\sim 8\%$. This result compares favorably to the $\pm 20\%$ precision guideline for portable lead-monitoring methods [17]. The XRF method shows a positive bias of 26.5% when compared to the reference method and fails to meet the NIOSH accuracy criterion.

This survey site allowed the collection of samples across a wide concentration range, which enabled us to determine how well the evaluated methods performed around and significantly above the occupational exposure limit. Table 2 shows the data concentration range obtained for each method. The results at the upper end in Figs. 1–3 appear to be more variable, and most samples required dilution (using either UE/ASV or atomic absorption spectrometry) when lead concentrations were above 1200 μg per sample.

To assess how well the UE/ASV and portable XRF method performed around the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) of 50 $\mu\text{g}/\text{m}^3$ for an 8 h time weighted average sample [19], all lead concentrations at or below 100 μg per sample (which corresponds to an air concentration of approximately two times the PEL) were compared to the reference laboratory method. Linear regression was performed on this subset of data. Figs. 4 and 5 show the slopes of the regression lines, the intercepts, and the R^2 values. Paired t -tests between the two field methods and the reference

Table 2
Lead concentration range (μg per sample) for each lead measurement method studied ($N = 68$)

Method	Minimum	Maximum	Mean	S.D. ^b
UE/ASV	14	1440	277	335
XRF	13	2210	365	457
FAAS-undigested	12	2200	300	404
FAAS-digested ^a	10	1400	290	350

^a Reference method.

^b Standard deviation.

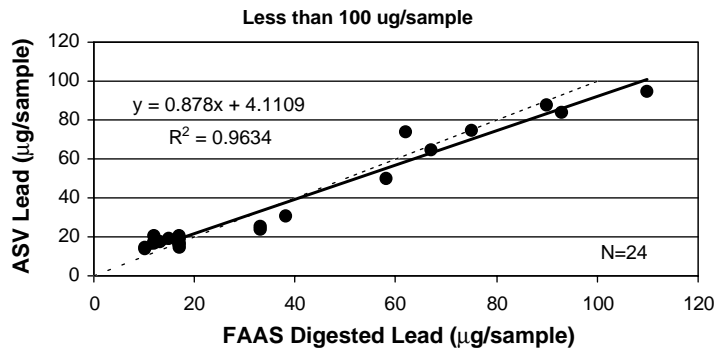


Fig. 4. Results between 10 and 100 μg Pb per sample from the UE/ASV method compared to FAAS-digested method. All other information is the same as given in Fig. 1.

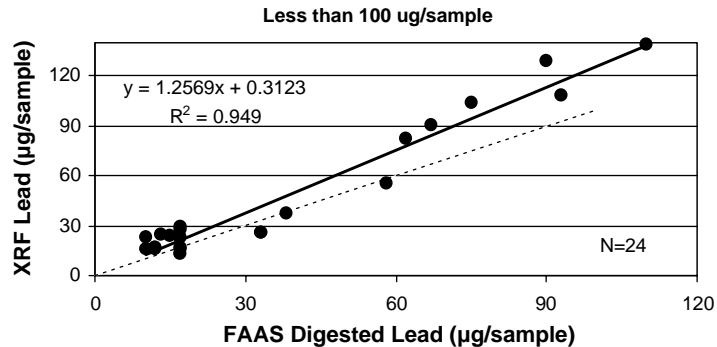


Fig. 5. Results between 10 and 100 μg Pb per sample from the portable XRF method compared to FAAS-digested method. All other information is the same as given in Fig. 2.

method using only concentrations at or below 100 μg Pb per sample paralleled the *t*-test results found using the complete data set. Specifically, there was no significant difference in results between the UE/ASV method and the reference method ($P = 0.84$); however, there was a significant difference between the portable XRF method and the reference method ($P < 0.001$). Even at the lower end of the scale, the XRF method consistently measured higher concentrations of lead than the other three methods.

5. Summary

Ultrasonic extraction of lead from air filter samples collected in the mining environment, followed by field-portable ASV, is a practical method for the on-site analysis of lead in workplace air. This method was highly correlated with the traditional laboratory method (NIOSH Method 7082), which involved microwave digestion of the filter in concentrated acid and subsequent analysis by FAAS. When compared to the FAAS acid-digested method, the

UE/ASV method is safer, since it does not require concentrated acids. Moreover, UE/ASV is less expensive, and offers simplicity and time savings. The ASV method outperformed the other three methods with respect to precision and bias, and was the only method that satisfied the NIOSH accuracy criterion. The method precision (R.S.D.) of ~8% was very good considering the wide concentration range of samples analyzed, and the bias was very close to zero.

The portable XRF method was less precise than the FAAS-undigested method, but more precise than the FAAS acid-digested method. While the XRF method did not meet the NIOSH accuracy criterion, this is likely due to the large positive bias between the XRF method and the FAAS acid-digested method. The bias appears to be due to the ability of XRF to detect lead in silicate particles that are not digestible unless hydrofluoric acid is used for extraction purposes. This implies that the analysis of lead by portable XRF method may be matrix-dependent. Note that the study which established the NIOSH screening method using portable XRF [7] was conducted in a construction setting, where the sample matrix differed from the one investigated in this study. Therefore, field-portable XRF, although a suitable screening method for airborne lead, should be used with the knowledge that it may overestimate airborne lead in mining and other settings where the lead may be bound to silicate particles. Further evaluation of this method against confirmatory analysis using hydrofluoric acid sample digestion is necessary to validate this finding.

Despite this apparent shortcoming, it should be kept in mind that field-portable XRF is very easy to use, and can be employed in the field by industrial hygienists to obtain rapid analyses to screen for lead in workplace air samples. This information can immediately be used to inform workers of possible overexposures so that corrective actions can be taken quickly. When used in this way, XRF can be useful to trigger control measures designed to reduce or eliminate excessive worker exposures to lead [20]. With traditional laboratory methods, workers may continue to be overexposed for days or weeks or more while the employer waits for the results. Since this is a nondestructive method, the filter samples can be sent to a fixed-site laboratory for confirmatory analysis, if needed.

The field-portable methods evaluated in this study can quickly and reliably provide airborne lead concentration data for mines and refining operations. Both on-site methods could be very useful in such applications as identifying potential overexposures and determining the effectiveness of intervention controls in near real-time. As a final point, the use of field screening methods can enable subsequent targeted sampling for compliance monitoring purposes [21].

Disclaimer

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

Acknowledgements

The authors thank Kurt Brumbaugh (NIOSH, Morgantown, WV) for his statistical guidance.

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