

# **APPLICATION OF A NOVEL SLURRY FURNACE AAS PROTOCOL FOR RAPID ASSESSMENT OF LEAD ENVIRONMENTAL CONTAMINATION**

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## **INTRODUCTION**

The rapid and accurate assessment of environmental hazards is the cornerstone in any legitimate program to protect both the environment and the public. Threats to the public health must be identified and rapidly eliminated by officials who have the proper information to make educated decisions. Instances of environmental injustice, where minority and low-income populations are subject to disproportionately high and adverse human health or environmental risks, need to be identified and corrected [1]. Analytical science plays the pivotal role in providing data for environmental decision-making, from site hazard assessment, through evaluation of remediation efforts, and finally in the appraisal of pollution prevention technology. Analytical scientists have been most successful in developing fast and accurate methods in the area of inorganic elemental analysis.

Public awareness of lead toxicity is not, as many think, a product of the environmental consciousness of the 1960s and 1970s. Lead poisoning in adults was first described in the second century B.C. Benjamin Franklin spoke of the "bad effects of lead taken inwardly" in 1786, and the first cases of lead poisoning in children were reported in Australia over 100 years ago. Unfortunately, the findings of investigators in the latter case that "painted walls and railings were the source of the lead and that biting of finger nails and sucking of fingers were the means of conveyance" were ignored by those in authority. When organic compounds of lead were introduced as an anti-knock ingredient for gasoline in 1923, similar concerns about public health were expressed by some in the scientific community. In 1925, the Surgeon General called experts from business,

labor and public health to assess the hazard of "ethyl gas", with the subsequent conclusion that there were no good grounds for prohibiting its use, provided that its distribution and use were controlled by proper regulations. The danger signs were ignored since there were no adequate measurement methods and standards to prove the case for lead toxicity at low concentration levels. Without hard scientific evidence, economic concerns prevailed. However, by the late 1950s evidence had built up, and paint manufacturers voluntarily limited the lead content of paint to 1%. But it was not until the 1970s that the U.S. government began to take an active role. There was a great deal of ground to cover, since pollution from lead had become widespread in the environment, arising from a number of sources, such as lead-based paint, leaded gasoline, and lead-based solder. Today, we face a three-fold challenge: (a) to identify environmentally-hazardous sources of lead and eliminate them; (b) to characterize lead toxicity and reduce lead levels in the general population; and (c) to recognize and rectify environmental injustice to minority and low-income populations. The need for rapid and accurate analytical technology has never been greater [2].

The ideal analytical method for the assessment of environmental contamination by toxic elements such as lead should be rapid and cost-effective, while retaining enough accuracy and precision to allow conclusions to be drawn from the data. Most analytical techniques do not meet these criteria. To obtain reasonably accurate results, they require the sample to be leached or dissolved in an acid media or fused at high temperature into a soluble form. Such sample preparation demands decrease sample throughput and thus lengthen the response time for environmental remediation, as well as requiring dedicated and expensive technician time. The few analytical methods that can be modified for direct elemental analysis of solids without pretreatment, such as x-ray fluorescence spectrometry, are limited by cost, matrix interferences, elemental coverage or sample size.

The slurry method of sample introduction for electrothermal atomic absorption spectrometry (slurry-ETAAS) provides a unique combination of minimal sample preparation, proven accuracy, low cost instrumentation, and rapid and unattended sample throughput that makes it ideal for the evaluation of large numbers of samples for toxic element contamination [3]. Slurry-ETAAS has been used successfully by a number of researchers for the determination of toxic elements in soils and sediments [4-6] and paints [7]. Lead is one of the elements most easily determined by the slurry method, since it readily extracts into the

solvent phase, thus maximizing precision and accuracy. Lead is also one of the most pervasive and toxic elements in the environment.

In this investigation, slurry-ETAAS was used to determine lead in samples of paint and soil from 53 parks and playgrounds in Arlington County, Virginia. The analysis results indicated a significant number of sites at which further evaluation is needed. The locations of high lead levels were compared to demographic information on income level to look for evidence of environmental injustice.

## EXPERIMENTAL

Soil was collected with a plastic utensil from several locations within each park and individual samples were combined to form a composite sample representing each park. Similarly, soil samples near streets adjacent to the parks were also collected and combined. The paint samples were taken from jungle gyms, slides, swings, benches, and posts within the parks and then combined to form a composite paint sample. Paint samples were taken with a stainless steel blade only from those playgrounds where equipment or structures had paint that was already chipped or peeling. Sampling tools were wiped with a lead-free baby-wipe between collections. A total of three composite samples (paint, park soil, and street soil) represented each playground or park, for a total of ~150 composite samples.

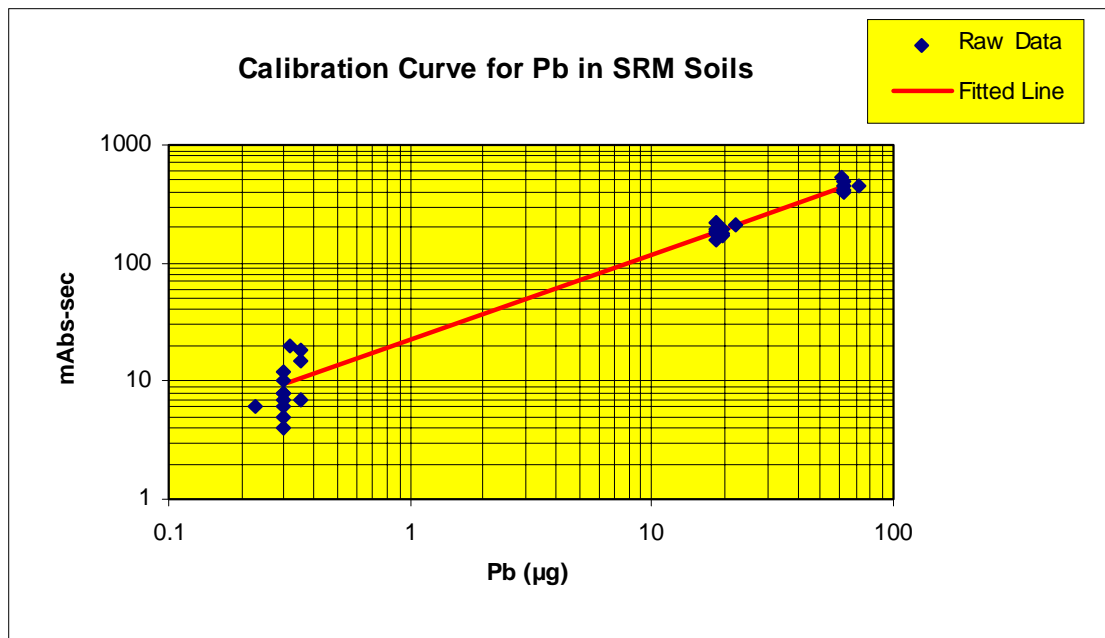


All samples were transferred to plastic bags and taken to the laboratory where they were crushed and mixed with a mortar and pestle. After homogenization, two subsamples weighing between 10 and 20 mg each were taken from each sample bag and placed into plastic autosampler cups, with the subsequent addition of 1 mL of a diluent solution consisting of 5% (v/v) HNO<sub>3</sub> (high-purity, sub-boiling distilled) and 0.05% (v/v) Triton X-100 surfactant (Rohm and Haas registered trademark for octyl phenoxy polyethoxyethanol).

Samples were analyzed using an atomic absorption spectrometer with Zeeman-effect background correction, a transversely heated graphite furnace atomizer, and an ultrasonic slurry mixing device. Peak area absorbance measurements were employed. The samples were suspended in the diluent solution using an ultrasonic probe and 20 µL of slurry was removed and introduced into an electrothermal atomizer for analysis. During the suspension, which is accomplished by ultrasonically disrupting the solution for 10 seconds, some of the sample matrix is dissolved in the acid, while the rest of the sample is suspended as small particles. For some elements, such as Pb, a very high fraction of the element will be dissolved during ultrasonic agitation in the acid media. But even if a very small fraction of the element is dissolved, as long as the particles are not larger than the diameter of the sampling capillary or too dense (so that they do not remain suspended for a few seconds after the ultrasonic disruption), both solution and particles are quantitatively transferred to the electrothermal atomizer by the micropipetor. Rather than the most sensitive lead line at 283.3 nm, a lower sensitivity spectral line of lead at 261.4 nm was used to provide a working range that would cover the concentrations of lead in soil and paint considered hazardous: > ~ 0.02% for lead in soil and > 0.5% for lead in paint.



Instrumental parameters for the analyses are shown in Table 1. A calibration curve was prepared from NIST Standard Reference Material Soils with concentrations of  $18.9 \pm 0.5 \mu\text{g Pb/g}$  (SRM 2709),  $1162 \pm 31 \mu\text{g Pb/g}$  (SRM 2711), and  $5532 \pm 80 \mu\text{g Pb/g}$  (SRM 2710) that were run before and after each sample set.



Sample throughput (duplicate measurements per sample) was approximately 15 samples per hour. The entire dedicated analysis time for  $\sim 400$  samples, standards, and controls was  $\sim 30$  hours (10 separate runs of 40 samples per run). After all analyses had been completed, Pb concentrations in the samples were calculated from a log-log plot of absorbance versus concentration, prepared from the pooled data from all analyses of the SRM soils and shown in Figure 2. Since both paint and soil samples from the parks and playgrounds were compared to the calibration curve prepared from the SRM soil samples, reference paint samples were also run blind as controls.

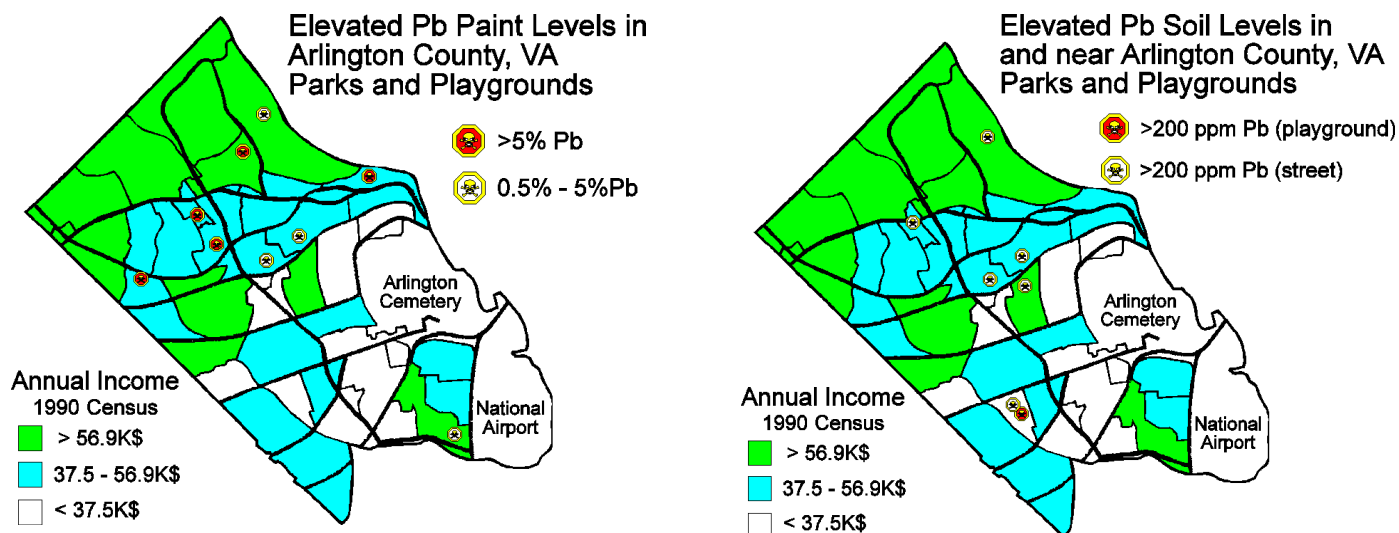
## RESULTS

Analysis results for the control paint samples are shown in Table 2. The method appears to provide adequate accuracy for survey analyses at lead concentrations greater than 0.01%, which is the range of primary concern.



Analysis results for the samples of paint and soil from the parks and playgrounds are shown in Table 3. In general, there was sufficient agreement between subsamples to draw conclusions, except in a very few cases at lower lead concentrations. Sample inhomogeneity probably accounts for these few results, since the samples were pooled from several locations within each park. No significant contamination from preparation or handling of the samples was detected. As noted in Table 3, soil lead concentrations were found to vary between 0 and ~700  $\mu\text{g Pb/g}$ , and paint lead concentrations varied from 0 to ~8 %Pb.

The concentrations of lead were compared to location and income level in the vicinity of the parks and playgrounds. Figures 3 and 4 show the distribution of sites where elevated lead in paint and lead in soil were found, as a function of annual income based on demographics from the 1990 census. In neither case does there appear to be evidence of environmental injustice. The majority of high lead level parks are in the medium income areas.



This survey was intended primarily as a test of the speed, accuracy, and precision of the slurry-ETAAS method when applied to a real analytical problem, and as a preliminary evaluation of lead poisoning dangers in public parks. Significant lead concentrations were found in some locations, and more thorough evaluation appears to be in order. The only significant limitation of the slurry-ETAAS method, as we used it, is the sequential nature of the atomic absorption measurement, which limits the range and speed of multielement analysis on

selected samples. It is quite adequate for rapid surveys when a limited number of known toxic elements are being investigated.

The accuracy base for slurry sampling combined with electrothermal atomization for atomic absorption is currently being established through international round-robin measurements [8]. Preliminary results show agreement within 20% of most participating laboratories on soil reference materials. While our study was conducted with a single-element AA instrument, multielement AA spectrometers are now available. The future of the slurry-ETAAS method lies with such instrumentation as well as in its combination with sensitive multielement techniques, such as inductively-coupled plasma mass spectrometry, for rapidly and accurately surveying toxic element contamination in the environment [9]. Not only can large numbers of elements be rapidly surveyed, but such methods allow for source identification through multiple element or isotope pattern recognition [10], providing policymakers with even more solid grounding to make just decisions on environmental issues.

## References:

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The authors thank the Perkin-Elmer Corporation for the use of the USS-100 ultrasonic mixing device. Mention of commercial equipment in this manuscript does not imply endorsement by the National Institute of Standards and Technology, nor does it imply that the equipment is the best suited for such use.

### Table 1. Instrumental Parameters

Instrument: Perkin-Elmer 5100ZL Atomic Absorption Spectrometer  
with USS-100 ultrasonic mixing device

Wavelength: 261.4 nm

Source: Hollow Cathode Lamp at 10 mA

Furnace Program:

Step	Temp	Ramp	Hold	Gas Flow	Other
1	110	1	20	250	Dry (stage 1)
2	130	5	30	250	Dry (stage 2)
3	400	10	20	250	Ashing
4	20	1	5	250	Cooldown
5	1600	0	10	0	Measure absorbance
6	2500	1	2	250	Cleanup



**Table 2. Results for Control Samples of Paint**

Analysis Designation	Identity or Source	Concentration (%Pb)	
		Reference	Determined
A	SRM 2582	0.0209 ± 0.0005	0.01
B	RTI <sup>a</sup>	0.14	0.16
C	RTI <sup>a</sup>	1.05	1.06
D	RTI <sup>a</sup>	0.85	0.98

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<sup>a</sup>Standards prepared by Research Triangle Institute, Research Triangle Park, NC

**Table 3. Summary of results for survey of lead contamination in Arlington County, Virginia parks and playgrounds. Results separated by a "-" are the average values for the two subsamples from each composite sample of soil or paint.**

Park Name	Income Level	Park Soil Pb (ppm)	Street Soil Pb (ppm)	Park Paint Pb (%)
Arlington Arts Center	high	11 - 14	100 - 430	0
Glencarlyn Park	high	7	110 - 150	0.1
Woodmont Center	high	2 - 11	70 - 110	-
East Falls Church Park	high	4 - 22	41 - 130	-
Edison Minipark	high	9 - 21	37 - 110	0.2
Stewart Park	high	22 - 30	47 - 56	-
Glebe Road Park	high	3 - 20	43 - 45	0.005 - 0.006
Fort Scott Park	high	7 - 8	11 - 58	2.5 - 3.7
Nottingham Elementary	high	6 - 25	23 - 28	0.004 - 0.006
Madison Manor Park	high	2 - 7	23 - 25	0.1 - 0.2
Madison Recreational Center	high	14 - 110	15 - 30	0.1 - 0.4
Greenbrier Park	high	17 - 56	14 - 20	0.0004 - 0.0008
Jamestown Playfield	high	7 - 10	4 - 11	0.5 - 0.6
Marcey Road Recreational Center	high	27 - 120	9 - 12	0.9 - 2.1
Taylor Park	high	5 - 31	3 - 7	4.4 - 8.1
Langston Community Center	middle	18 - 180	320 - 580	0.005 - 0.008
Quincy Street Playground	middle	36 - 66	340 - 490	0.5 - 0.7
Clarendon Playground	middle	4 - 5	90 - 320	0.7
Dawson Recreation Center	middle	1	32 - 270	5.4 - 6.2
Lacey Woods Park	middle	10 - 220	96 - 210	0.0005 - 0.0007
Barcroft Park and Playground	middle	21 - 31	100 - 180	-
Jackson School	middle	56 - 170	110	0.2 - 0.6
Alcova Heights Park	middle	9 - 26	80 - 110	0
Lee Recreation Center	middle	7 - 9	86	0.001 - 0.006
Lyon Village Playground	middle	27 - 38	40 - 130	-
Abingdon School	middle	<1	15 - 140	-
High View Park	middle	4 - 62	58 - 88	4.5 - 7.8
Hayes Playground	middle	11 - 14	50 - 92	-
Eades Playground	middle	12	25 - 120	-
Parkhurst Playground	middle	7	35 - 74	0.6 - 0.7
Woodlawn Park	middle	20 - 27	31 - 65	6.5 - 7.8
Virginia Highlands Park	middle	4 - 15	19 - 56	-
Utah Field Park	middle	7	22 - 37	-
Bon Air Park	middle	7 - 9	15 - 30	4.9 - 7.3
McKinley School	middle	6 - 25	17 - 21	-
Westover Park	middle	12 - 27	11 - 23	0.0002 - 0.0007
Butler Holmes Playground	middle	6 - 19	7 - 16	0.1 - 0.3
Wilson Adult Center	middle	28 - 40	5 - 11	0.0008 - 0.0009
Doctor's Run Park	low	9 - 660	230 - 260	0.3
Carver Community Park	low	2 - 5	180 - 200	0.0001 - 0.001
Clay Playground	low	1 - 28	95 - 280	0.0001 - 0.0002
Fort Bernard Park	low	4 - 9	130 - 160	0.02
Walter Reed Recreational Center	low	2 - 3	120 - 160	-
Troy Playground	low	7 - 9	94	0.1 - 0.7
Patrick Henry Playground	low	7 - 12	60 - 86	0.1
Shirley Park	low	5	28 - 110	-
Nauck Playground	low	19 - 89	21 - 88	-
Lubber Run Community Center	low	4	34 - 60	0.009 - 0.02
Arlington Heights Park	low	5 - 51	32 - 37	-
Towers Park	low	27 - 50	20 - 46	0
Rocky Run Playground	low	6 - 11	29 - 40	-
Long Branch Elementary	low	<1	17 - 28	-
Drew Community Center	low	1	9 - 26	-