

Laboratory Procedure Manual

Analyte: **Lead**

Matrix: **Dust Wipes**

Method: **Modification of the Automated AAll-25
Colorimetric method**

Method No.: **Nitric and Hydrochloric Acid Digestion
followed by Atomic Absorption
Spectroscopy Analysis**

Revised:

as performed by: *Department of Environmental Services
University of Cincinnati*

Contact: *Ms. Sandy Roda
1-513-558-1705*

Important Information for Users

The University of Cincinnati periodically refines these laboratory methods. It is the responsibility of the user to contact the person listed on the title page of each write-up before using the analytical method to find out whether any changes have been made and what revisions, if any, have been incorporated.

Public Release Data Set Information

This document details the Lab Protocol for NHANES 2003–2004 data.

A tabular list of the released analytes follows:

Lab Number	Analyte	SAS Label
lab20_c	LBDDWS	Lead dust window ($\mu\text{g}/\text{sq ft}$)
	LBXDFS	Floor, GFAAS ($\mu\text{g}/\text{sq ft}$)
	LBDFSF	Floor, FAAS ($\mu\text{g}/\text{sq ft}$)
	LBDDFSLC	Floor (GFAAS) comment code
	LBDDD3LC	Floor (FAAS) comment code
	LBDDWSLC	Window comment code

1. SUMMARY OF TEST PRINCIPAL AND CLINICAL RELEVANCE

The preparation procedure for dust wipe sample digestion involves the quantitative transfer of the sample from the container into a beaker for subsequent addition of nitric and hydrochloric acids and hot plate heating. The procedure is described in the Appendix of the Guidelines for the Evaluation and Control of Lead-Based Hazards in Housing (1). The technique does not involve complete digestion of the sample but leaching of the lead (Pb) from the collected dust. Recovery of the method is based and evaluated on the results of matrix (wipe) spiked National Institute of Standards and Technology (NIST) quality control samples. The lead content of the digestate is determined by using a Perkin-Elmer Flame- Atomic Absorption Spectrometer (FAAS) Model 5000 or 5100 for all window dust wipe samples and a PerkinElmer Graphite Furnace Atomic Absorption Spectrometer (GFAAS) Model 5100 for all floor-dust wipe samples. However, floor-dust samples whose values are found to be 5 µg or greater by GFAAS are re-analyzed by FAAS and that value reported.

2. SPECIAL SAFETY PRECAUTIONS

Technical staff while working in the laboratory must wear gloves, lab coat and protective glasses. Because of the use of acids, the laboratories are supplied with spill kits, eye washes, and showers. Staff members are required to attend a yearly OSHA training on "Hazard Communication." Cleanliness and organization is enforced to prevent contamination to individuals and samples and to prevent the occurrence of any safety hazards.

The University of Cincinnati has a written chemical hygiene plan for the laboratories that follows applicable federal, state and local regulations regarding safety and health.

3. COMPUTERIZATION; DATA SYSTEM MANAGEMENT

The technician responsible for the analysis performs and checks all raw data transfers from worksheets. A second technician confirms the accuracy of these entries. In addition, sample quality, duplication of results, deviations from normal, and any other information obtained during the processing or analysis of the samples are evaluated with respect to expected performance.

After all within-lab checking of raw data sheets and distribution forms have been completed, the distribution office will receive the final results of the analysis. Report forms are generated using the file format obtained from the NHANES laboratory. Once entered, the information is double checked, reviewed by the laboratory director, and electronically sent to the NHANES laboratory. All paperwork associated with the samples and their analysis is organized in a data packet and filed. Results after reported are transferred to a disk and archived in the director's office.

4. SPECIMEN COLLECTION, STORAGE, AND HANDLING PROCEDURES; CRITERIA FOR SAMPLE REJECTION

Dust wipe samples for Pb are collected by NHANES staff according to defined procedures. Samples are contained in 50-ml polypropylene tubes, packaged in sturdy containers and shipped overnight to the laboratory. A visual evaluation of the sample container and its contents is done at the time of sample receipt at the laboratory. This includes an assessment of the condition of the shipping container or box, confirmation of the number of samples listed on the chain-of-custody form, the actual sample identity information compared to the chain-of-custody form, and the condition of the sample tube and its contents. Any abnormalities are documented at that time.

Dust wipe samples may be stored at room temperature indefinitely or until analyzed. Sample digestates, if tightly capped, are normally held by the laboratory for six months. Dust wipe samples will be rejected or not analyzed only if the integrity of the container has been compromised, such as found uncapped, or if the tube has been badly damaged.

5. PROCEDURES FOR MICROSCOPIC EXAMINATIONS; CRITERIA FOR REJECTION OF INADEQUATELY PREPARED SLIDES

Not applicable for this procedure.

6. PREPARATION OF REAGENTS, CALIBRATORS (STANDARDS), CONTROLS, AND ALL OTHER MATERIALS; EQUIPMENT AND INSTRUMENTATION

A. DIGESTION PROCEDURE REAGENTS AND CONTROLS

- (1) Concentrated Nitric acid (Reagent grade)
- (2) Concentrated Hydrochloric acid (Reagent grade)
- (3) Distilled-Deionized Water (DDW)
- (4) Reagent blank – DDW subjected to entire digestion and analysis procedure.
- (5) Method blank – digestion and analysis of a blank wipe of the same kind and from the same lot # of wipes used to collect the field samples.
- (6) Reagent control sample – digestion and analysis of DDW that has been spiked with a known amount of a NIST SRM.
- (7) Method control sample - digestion and analysis of a blank wipe of the same kind and from the same lot # of wipes used to collect the field samples that has been spiked with a known amount of a NIST SRM.

B. ANALYSIS REAGENTS AND CONTROLS

(1) FAAS Analysis

- (a) Calibration Standards – the following volumes of a 1000 ppm Certified Standard solution, Fisher Scientific are added to each of six 100-ml volumetric flasks and taken to volume with 1 M HNO₃:

Pb (ppm)	Volume (ml) of Stock Added
0	0
0.5	0.05
1	0.1
5	0.5
7	0.7
10	1

- (b) 1 M Nitric Acid – 64 ml of Reagent grade HNO₃ q.s. to 1 L with DDW, used for the dilution of samples outside of the calibration range.

(2) GFAAS Analysis

- (a) Calibration Standards – the following volumes of a 1000 ppm Certified Standard solution, Fisher Scientific are added to each of six 100-ml volumetric flasks and taken to volume with 1 M HNO₃:

Pb (ppb)	Volume (ml) of Stock Added
0	0
2	0.2
8	0.8
15	1.5
25	2.5
40	4.0

- (b) 1 M Nitric Acid - 64 ml of Reagent grade HNO₃ q.s. to 1 L with DDW, used for the dilution of samples and standards.
- (c) 1% NH₄H₂PO₄ - 1 g in 100 ml DDW
- (d) 0.05% Mg(NO₃)₂ - 0.05 g in 100 ml DDW
- (e) QC samples using Spex Standard – 0.2 ml of standard diluted to 100 ml with 1 M HNO₃ = 20 ppb Pb; 0.1 ml of standard diluted to 100 ml with 1 M HNO₃ = 10 ppb Pb.
- (f) All samples are initially diluted by a factor of 7 to avoid matrix interference – 3 ml of 1 M HNO₃ plus 0.5 ml of sample.

C. INSTRUMENTATION

(1) FAAS instrumentation

FAAS analysis is performed on a PerkinElmer Model 5000 or 5100 atomic absorption spectrometer using an EDL power supply or HCL source lamp. The wavelength setting for Pb is 283.3 nm. Line pressure settings are preset at approximately 50–64 for air and 20–30 for acetylene. Manual aspiration of the samples is performed.

(2) GFAAS instrumentation

The analysis for Pb in floor-dust wipe samples is performed on a Perkin-Elmer Model 5100 graphite-furnace atomic absorption spectrometer with Zeeman background correction. The system is microcomputer controlled with a CRT display, keyboard, and AS-70 Autosampler. Virtually all operating parameters and functions for the spectrometer and the graphite-furnace are entered via the keyboard. The following program is used for the analysis of Pb in dust-wipe samples by graphite-furnace:

Wavelength (nm):	283.3	Max sig. figures:	5
Slit width:	0.7	Read Time (sec):	3.0
Signal type:	Zeeman	Read delay (sec):	0.0
Signal Measurement:	Peak area	BOC time (sec):	2.0
Pb linear, calculated intercept		Calibration units:	ppb
Sample units:	ppb	Max decimal places:	4

Furnace Conditions						
Step#	Temp(°C)	Ramp Time	Hold Time	Flow Time	Gas Type	Read Step
1	120	1	20	250	Normal	
2	140	5	30	250	Normal	
3	900	10	20	250	Normal	
4	1700	0	5	0	Normal	X
5	2400	1	2	250	Normal	

7. CALIBRATION AND CALIBRATION VERIFICATION PROCEDURES

Dust-wipe sample digestates are analyzed using either a Perkin-Elmer Model 5000 or 5100 Flame Atomic Absorption Spectrometers (FAAS). Working standards are prepared from standard solution stocks using a 1 M HNO₃ matrix. A midrange control standard and a calibration blank are evaluated no less than every 10 samples during a run. If there is more than a 5% relative percent difference to the previous standard, the entire set of standards is re-examined. If necessary, the subset of samples subject to the disagreement is re-run after a review of methods and procedures, and after corrections have been made so that standards are verified within 5% RPD. Reagent blanks, controls and NIST standards are incorporated into each preparation of samples. The concentration of all controls must be within +10% of the established value. If not, the samples are re-analyzed.

The actual run order of samples analyzed by FAAS or GFAAS follows:

Sample No.	Sample ID	Description
1	ICB	Calibration Blank
2–4	Low Std. - High Std.	Calibration Standards
5	ICB	Calibration Blank
6	ICV	Different stock, Conc. Near mid-point
7	High Std.	Calibration Std.
8	CCB	Calibration Blank
9	ICS (ICP)	Interference check sample
10	CCB	Calibration Blank
11	CCV	Intermed. Calibration Std.
12	CCB	Calibration Blank
13–22	Samples	Digestates
23	CCV	Intermed. Calibration Std
24	CCB	Calibration Blank
25–34	Samples	Digestates
35	ICS (ICP)	Interference check sample
36	CCB	Calibration Blank
37	CCV	Intermed. Calibration Std
38	CCB	Calibration Blank

8. PROCEDURE OPERATING INSTRUCTIONS; CALCULATIONS; INTERPRETATION OF RESULTS

A. SAMPLE DIGESTION PROCEDURE

- (1) Remove the wipe from its container and place into a 50–100 ml glass beaker. Quantitatively rinse the container transferring the contents to the beaker. Add DDW to cover the wipe (~10 ml). Use a glass rod and stir the wipe to open it. Rinse the glass rod with DDW and add to the beaker.
- (2) Add two ml of concentrated HNO_3 and 2 ml of concentrated HCL.
- (3) Gently heat at 100°C for 20–30 minutes under reflux.
- (4) Cool and transfer all contents to a 50-ml graduated tube. Rinse any bulk material several times and gently squeezing with a glass rod while pouring the solution over into graduated tube.
- (5) Add DDW to 50 ml, cap and mix well.
- (6) If need be, prior to analysis filter a portion of the sample through ashless filter paper into a clean tube or centrifuge the original sample at 9000 rotations per minute (rpm) for 20 minutes.
- (7) The final digestate is analyzed by either FAAS or GFAAS.

B. ANALYSIS PROCEDURE

(1) FAAS

- (a) Turn the instrument on and light the hollow cathode lamp or electrodeless discharge lamp. Allow the instrument to warm up for 45 minutes prior to use.
- (b) Adjust the wattage on the HCL to that recommended on the lamp and allow it to warm up for 20 minutes prior to use. Adjust the milliamps to the proper level.
- (c) Tweak up the wavelength (283.3nm) for maximum light throughput (energy).
- (d) Check the following line pressures: air = 50–64; acetylene = 20–30. Ignite the burner and allow a 5-minute warm-up time.
- (e) Optimize the burner position for maximum absorbance while aspirating a 10 ppm solution of lead in 1 M HNO_3 .
- (f) If applicable start the chart recorder (20 mm/min, 10 mv).
- (g) Start analyzing standards and samples according to standard run order. Allow enough time in between samples to achieve baseline.
- (h) The standard analyzed after every 10 samples should agree within 5% of the previous one. If not, re-calibrate.
- (i) Any samples over 9 ppm should be set aside for dilution.
- (j) An analytical duplicate should be analyzed after every 25 samples. One sample should be selected for recovery after every 20 samples.

(2) GFAAS

- (a) Turn on the power switch for the PE 5100 ZL Zeeman Furnace Module and the lamp power supply. Lamp requires a 15-minute warm-up time. Lamp alignment is pre-set.
- (b) Turn on the computer and printer. Cooling water should be on at this point. Turn on the Argon gas.
- (c) Open the WinLab software and identify the GFAAS computer program for Pb in dust wipes.
- (d) Clean the graphite tube with Q-tips and Kimwipes or replace the tube if necessary. Check the windows of the furnace to make sure they are clean.
- (e) All instrument settings are computer controlled. The wavelength is set at 283.3 nm.
- (f) Enter sample positions and identities on the computer following the standard run order for calibration standards, samples, blanks and QC checks. The instrument is programmed to add the matrix modifier and analyze samples for duplicates and recoveries.

- (g) Load the auto-sampler and check the HCL lamp energy reading. The energy should range between 70 and 73. Check the alignment of the sampling tip.
- (h) Start the program for analysis of samples to begin.
- (i) Calibration check samples analyzed outside of the established limits will initiate instrument re-calibration.

C. CALCULATIONS AND REPORTING

- (1) Sample concentration is derived using a linear regression equation of the standards and their absorbance readings.
- (2) The correlation coefficient for the standard curve must be 0.995 or better.
- (3) Specimens are repeated if their analytical duplicates differ by more than +10 RPD.
- (4) All samples whose results are greater than 9 ppm are diluted and re-analyzed.
- (5) The Method Detection Limit (MDL) is 2 µg by FAAS and 0.16 µg for GFAAS. Results below the MDL are reported, however, qualified to indicate that they are lower than the MDL.

9. REPORTABLE RANGE OF RESULTS

All window dust wipe results are analyzed by FAAS. Floor samples are first analyzed by GFAAS. If the result is greater than or equal to 5 µg, the sample is re-analyzed by FAAS and that value reported. All results by FAAS greater than 9 ppm are diluted and re-analyzed.

10. QUALITY CONTROL (QC) PROCEDURES

External and internal quality control procedures are implemented for the analysis of the NHANES IV dust wipe samples. Fictitiously identified samples of known Pb content are sent to the lab by the field staff. Within the lab QC and blanks are intermixed in the samples to assess each stage of sample prep and analysis.

Each digestion set contains approximately 20 samples and the following quality control:

- (1) Reagent blank – water and acids.
- (2) Method blank – water, acids and a wipe from the same lot number of material as used to collect the samples.
- (3) Reagent spike – standard, water and acids.
- (4) Method spike – standard, water, acids and a wipe from the same lot number of material as used to collect the samples.

Each analytical run includes an analytical duplicate and analytical spike to determine percent recovery. Depending on the number of samples analyzed, there may be an additional duplicate or percent recovery sample added to the run.

All blanks must be less than or equal to 4 µg of lead or 2× the method detection limit (2 µg). On the FAAS, all standards and percent recovery samples must be within +10% of the standard value. These reflect the laboratory's own internal QC criteria. In addition, QC charts are maintained so that performance on these samples can be both documented and evaluated. Previous experience has shown that the laboratories' established mean for the method is comparable to the NIST value of an SRM. However the means are calculated, the NIST value is used to establish the acceptable limits. The analysis is concluded to be out of control if any two or more of the following occurs within one set of samples:

- (1) One point outside of the control limits
- (2) Two points falling within the warning range
- (3) An unusual or nonrandom pattern in the data

- (4) One or more points near a warning or control limit

(If this occurs the samples will be re-analyzed first before being designated as out of control.)

11. REMEDIAL ACTION IF CALIBRATION OR QC SYSTEMS FAIL TO MEET ACCEPTABLE CRITERIA

Dust wipe samples consist of only one sample to digest and analyze. Technical staff must use extreme care when handling and analyzing these samples. Once the sample has been digested, however, enough digestate is available for several analyses. If QC unacceptable criteria persist after re-analysis of the digestates, the results for all samples would be qualified as being in possible error.

12. LIMITATIONS OF METHOD; INTERFERING SUBSTANCES AND CONDITIONS

As with all trace metal, sampling and analysis contamination of the samples must be avoided. The digestion procedure used for dust wipes is typical of others used by laboratories for this matrix. The methods do not involve complete digestion of the sample, however, and thus may not always extract all of the available Pb from the sample. Addition of hydrogen peroxide in this method has demonstrated a possible interference or suppression of signal during the analysis.

13. REFERENCE RANGES (NORMAL VALUES)

According to the 1995 Guidelines for the Evaluation and Control of Lead-Based Paint Hazards in Housing, the Federal Lead Standards are defined as 100 $\mu\text{g}/\text{ft}^2$ for floors and 500 $\mu\text{g}/\text{ft}^2$ for interior window sills. New guidelines have not been officially set at this time; however, it is expected that the floor standard will be lowered to 40 $\mu\text{g}/\text{ft}^2$.

14. CRITICAL CALL RESULTS

This is not applicable for the dust-wipe sample results.

15. SPECIMEN STORAGE AND HANDLING DURING TESTING

Specimen containers should remain tightly capped until opened for analysis. Samples can be stored in a cool dry place indefinitely prior to analysis. Once digested, the acidic digestate will remain stable unless some leakage of the cap allows sample evaporation or the acid medium causes deterioration of the container. Our laboratory's designated holding time for dust-wipe digestates is 6 months.

16. ALTERNATE METHODS FOR PERFORMING TEST OR STORING SPECIMENT IF TEST FAILS

Other digestion methods are acceptable for dust-wipe samples. Instrumental analysis by ICP is also acceptable. This should never be necessary because the laboratory is equipped with 2 FAAS and 2 GFAAS. We have multiple digestion laboratories and maintain service contracts with PerkinElmer on our instruments.

17. TEST RESULT REPORTING SYSTEM; PROTOCOL FOR REPORTING CRITICAL CALLS (IF APPLICABLE)

This is not applicable for the dust wipe sample results.

18. TRANSFER OR REFERRAL OF SPECIMENS; PROCEDURES FOR SPECIMEN ACCOUNTABILITY AND TRACKING

Sample chain-of-custody procedures are a very important part of this lab's operation. Acceptance, progression, and release of results for all samples are documented. When samples are delivered to the lab a signature is received from the shipping agent and receipt acknowledged by the laboratory person in charge of the distribution office. Listed with the signatures is the type of sample, sample names and the analysis requested. Date and time of acceptance is also recorded.

Samples are then logged on to the appropriate distribution form and given a lab number assignment. Individual packets are made up for each group of samples to form the data packets for the samples. These accompany the samples to the lab for analysis. Prior to this the laboratory technician signs for receipt of the samples and progression through the labs is continually tracked on the distribution form. Results of all sample analysis are registered on the original distribution form which, after recheck, is returned to the distribution office. Using the same form as used for sample sign out, the results are signed back in.

The final results are prepared using the electronic file from the NHANES lab. Once the information is entered it is rechecked and then e-mailed back to the NHANES staff. Data that has been entered and sent is then copied to a disk and filed in the director's office. Data packets are stored in files within the distribution office of the lab and will be kept for 10 years.

REFERENCES

1. United States Department of Housing and Urban Development, Guidelines for the Evaluation and Control of Lead-Based Paint Hazards in Housing, Washington, D.C. June, 1995.
2. Perkin-Elmer Model 5100ZL User Documentation; Publication B3208.10; Release 1.2/Sept. 92.