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TITLE: ANALYSIS OF DUST AND SOIL FOR LEAD, CADMIUM, AND CHROMIUM

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ANALYSIS OF DUST AND SOIL FOR LEAD, CADMIUM, AND CHROMIUM

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1.0 SCOPE AND APPLICATION

House dust can be a significant source of metal exposure, especially lead. Sources of lead in house dust include soil tracked or blown in from outdoors and lead-base paint chips. Wipe sampling will be conducted to determine the metals content of house dust on a Fg/cm^2 basis. Soil is another potential source of exposure to heavy metals and will be analyzed for its content as well.

This protocol describes the methodology and quality control measures that will be undertaken in the analysis by inductively coupled plasma/mass spectrometry of dust wipes, wet wipes, soil and the rug/mat for metals. The data will be used to assess the potential exposure to heavy metals through the aforementioned media. It is solely designed for a survey type study. There will be three metals examined in this study; Pb, Cd and Cr.

2.0 METHOD SUMMARY

The samples will be extracted with a 10% or greater concentration of ultra-pure nitric acid and diluted to a final concentration of 2% or less total acid. The extraction will be carried out in a pressurized microwave for the dust and soil samples and in an ultra-sonic bath for the rug/mat samples. The analysis will be carried out by inductively coupled plasma/mass spectrometry using calibration curves for concentration determinations. A soon to be adopted EPA method 6020 will be used as the general guideline for the analysis.

3.0 POTENTIAL INTERFERENCES

Lead is the primary analyte of interest. It has one isotope in common with mercury which is a potential interfering species. The raw data for this isotope can easily be corrected by either background subtraction or isotope dilution. Cadmium has potential interferences from tin. Although the background subtraction algorithm is a bit more complicated than the correction applied to lead, it can also be corrected in a similar fashion. Chromium has a major molecular interfering species of argon oxide and argon carbide. We can minimize the creation of these species and blank subtract to correct for these. The signal created by these

molecular isobars is very stable and has been easy to compensate for in work previously carried out by this lab.

4.0 SAFETY

The sample themselves present no inherent safety risks. The extraction process used to liberate the metals from their matrices involve high pressure reaction vessels and concentrated acid solutions. All of the standard precautions; specifically safety glasses, lab coats, rubber gloves and hood work will be employed in the processing of these samples.

5.0 EQUIPMENT

Extraction

1. Polysulphone Tubes (Oak Ridge)
2. CEM Microwave Vessels, Liners, Teflon Membranes
3. Ultra-Sonic Bath

Analysis

1. Polyethylene auto sampler test tubes
2. ICP/MS PQS Fisons Instruments
3. Class A volumetric glassware

6.0 REAGENTS AND STANDARDS

Extraction

1. 18 Megaohm Type 1 water
2. Double Distilled Nitric Acid (Currently purchased from High Purity Standards of South Carolina with a Certificate of Analysis)

Analysis

1. Multi-Element custom mix Standard (from High Purity Standards of South Carolina)
2. NIST SRM 3171 Multielement Mix A

3. NIST SRM 3128 Lead Solution
4. NIST SRM 2709 San Joaquin Soil
5. NIST SRM 1648 Urban Particulate
6. NIST SRM 2676c Metals on filter media
7. 18 Megaohm Type 1 water
8. Any additional SRM's provided by NIST

The standards, QC and calibration will be prepared in accordance with EPA Method 200.8.

7.0 SAMPLE STORAGE

Wipe Samples

Upon delivery to the lab, the wipe samples will be laid out in a dust free chamber in the weighing room for 48 hours to dry. The envelope containing the sample will be placed in the chamber on the foil. After the drying period, the final mass of the filters will be measured in accordance with the standard operating procedure for weighing wipe sample filter media.

The samples will then be stored in plastic zip-lock storage bags until they are prepared for analysis. Once extracted the samples will be stored as solutions in polyethylene or like bottles until analysis. All samples will be stored under cold room conditions until they are dried.

Soil Samples

Upon delivery to the lab the samples will be allowed to dry by opening the sample storage bag in a humidity controlled environment room for at least 48 hrs. The samples will be mixed periodically by closing the bag and shaking.

Carpet Samples

Upon delivery to the lab the samples will be placed in a plastic bag until they are ready to be sampled.

8.0 QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

Quality Assurance

1. The EOHSI laboratory will participate in a round robin studies if deemed appropriate and necessary for wipe sample analysis of lead. This would include the analysis of any performance samples provided by NIST.
2. The quality control officer will conduct an audit of the quality control measures involved with the analysis. This will occur periodically throughout the study.

Quality Control

1. A standard operating procedure will be followed for weighing the filter media.
2. Initial and final weights of the sampling media will be recorded in a notebook.
3. Samples of the sampling media will be analyzed for background lead, cadmium and chromium levels prior to use.
4. A standard operating procedure will be followed for analysis of the wipe samples.
5. All sample collection apparatus will be cleaned prior to implementation in the field in accordance with the standard operating procedure for cleaning labware.
6. All samples will be labeled to ensure proper identification.
7. All data relevant to the collection of the sample will be recorded on a data sheet.
8. A custody record will accompany each sample throughout its collection, handling, and analysis.
9. An analytical protocol based on EPA Method 200.8 will be followed for sample analysis.
10. A series of calibration standards will be analyzed prior to and immediately following analysis of the samples.
11. A control standard will be analyzed after every 10 samples.

12. Control charts will be employed to ensure the precision of the analytical method is within acceptable limits based on analysis of the control standard. They will be updated after every 15th sample run.
13. Multiple isotopes will be used for cadmium and lead.
14. Field blanks will be collected and analyzed.
15. Lab blanks will be analyzed at least one per analytical run.
16. Reagent blanks will be analyzed at least one per run.
19. Standard reference materials will be analyzed to ensure the accuracy of the analytical method such as NIST standard reference material 2709.
20. The analyst will monitor the results of the QC sample checks and will reject any data acquired when a QC sample is greater than 20% from the certified value or 10% from a limit of the range of certified values whichever is greater.
21. A permanent record of calibration data for each analytical run will be kept.
22. Records of the ICP/MS operating parameters for each run will be recorded in a log book.
23. A record of spectrometer maintenance will be kept in a log book.
24. A permanent record of all sample analysis, including blanks, duplicates, spiked samples, and standard reference materials, will be kept.

9.0 SAMPLE EXTRACTION AND CLEANUP

Sample Preparation

Surface Soil: The soil samples will be prepared by drying for 24 hrs in a controlled humidity room then a 0.5 gram sample will be analytically weighted into a polysulphone tube and extracted as specified below.

Settled Dust: The settled dust will be removed from the surface with the LWW wipe sampler. Side by side samples will be collected. One for Cr, Cd and Lead and one to be sent to RTI for As analysis. The filter will be analyzed in the same fashion as the wipe samples collected from field as listed below. (Note, this is an experimental protocol with details and specific SOPs to be determined)

Wipe samples: The wipe samples will be dried for 24 hrs in a controlled humidity room, weighted and extracted by the procedure listed below.

Carpet Samples: A subsample of the carpet will be removed from the main carpet and shipped to RTI for As analysis. The remaining portion will be sampled by removing a second subsample from the main carpet and extracting in a dilute acid solution in an ultra-sonic bath. (Note, this is an experimental protocol with details and specific SOPs to be determined).

Extraction

Reagents: concentrated spectrographic grade nitric acid and Type I reagent grade water.

Extracting Solution: Prepare the extraction solution adding 200 mL of HNO_3 to 800 mL of Type I water. Cool the solution.

Extraction Procedure

1. Place the sample in a polysulfone Oak Ridge centrifuge tube.
2. Dispense 10 mL of extraction solution into the centrifuge tube.
3. Cap the tube tightly.
4. Dispense 31 mL of Type I water into a 120 mL Teflon microwave digestion vessel.
5. Place the Oak Ridge centrifuge tube containing the sample in the digestion vessel.
6. Attach a new rupture membrane to the safety valve and cap on the vessel.
7. Fill the microwave turntable with 12 vessels containing the centrifuge tubes. and place the turntable in the oven.
8. Activate the "on" switch and the "turntable" switch.
9. Set the exhaust fan to maximum speed.
10. Program the microwave oven for a time of 23 minutes and a power of 82% (522 watts).
11. Press the "start" button.
12. At the end of the program, remove the turntable containing the microwave vessels and cool it in tap water for 10 minutes.
13. Open the microwave vessels and discard the water they contain.

14. Open the Oak Ridge centrifuge tubes and add 10 mL of Type I water.
15. Cap the tubes tightly and mechanically shake for 5 minutes.
16. Centrifuge 25 minutes at 2000 rpm.
17. Open the centrifuge tubes and decant or pipette off the clear solution into an acid cleaned scintillation vial for analysis.
18. Use a sample volume of 20 mL to calculate analytical results.

Standard Operating Procedure Labware Cleaning

A. Cleaning Solutions

1. Soap Solution: Prepare a solution of laboratory detergent (SPARKLEEN or equivalent) in deionized water in accordance with the manufacturer's directions.
2. Prepare a 20% (v/v) acid cleaning solution from reagent grade nitric acid and deionized water.

B. Cleaning Procedure

All labware will be cleaned prior to use as outlined in the following procedure:

1. If labware contains organic material or significant sample residue soak labware for a minimum of 2 hours in the soap solution if it does not proceed directly to step 3.
2. Wash labware thoroughly using clean paper towels and rinse 3 times in deionized water.
3. Soak/fill labware with acid cleaning solution and allow to stand for a minimum of 4 hours.
4. Empty the acid cleaning solution from the labware and rinse 5 times with Type I reagent grade water.
5. Store all volumetric labware filled with acidified (2% v/v HNO3) type I water.
6. Allow all other labware to dry in a clean, dry, dust-free environment.

10.0 CALIBRATION AND STANDARDIZATION

Calibration

The spectrophotometer will be calibrated by analyzing a series of 5 standards prepared from a certified lead reference solution traceable to NIST reference materials. The concentrations of the standards will be 1, 3, 5, 7, and 10 µg Pb Cd and Cr/l. Standards will also be analyzed at 20, 50 and 100 µg Pb, Cd and Cr/l.

11.0 ANALYSIS PROCEDURE

Analysis

1. PROTOCOL: The primary method of analysis for dust and soil samples will be by ICP/MS analysis like EPA Method 200.8.
2. INSTRUMENTATION: Analysis will be performed using a VG Fisons Plasma Quad Model (PQS)Inductively Coupled Plasma spectrometer.
3. Sample, reagent and standard blanks will be run with each sample data set and subtracted from the appropriate signals when they are found to be significant. (>10% of the lowest measurable sample concentration)
4. QUALITY CONTROL: An NIST calibration standard at nominal concentration for the analytes of interest, will be run after every 10 samples to ensure that the analytical precision remains within predetermined limits.

12.0 METHOD PERFORMANCE

The method detection limit estimated based on the sensitivity of the measurement (reported as the slope of the calibration curve) and a 3 sigma of 15 blank measurements. The data's quality will be evaluated at the end of each sample run. Sample runs in which the QC checks differ by more than 20% from their certified value or more than 10% from one of the value limits will be repeated. The analyst will make this determination. Questionable

situations will be reviewed with the quality assurance officer and a final decision rendered at that time. Performance charts will be maintained by the analyst and updated after every 15th data set acquired. These charts will be review by the QA officer on a monthly basis.

13.0 DATA MANAGEMENT

The data will be processed by the computer program which operates the instrument. The raw data as well as the final reported concentrations will be examined after every run by the operator and periodically reviewed by the quality assurance officer. The QA officer will also review any run which is thought to be suspect by the operator. Raw data as well as the calculated concentrations of the sample solutions will be stored on floppy disk for retrieval at any time.

The dilution factors for the individual solid samples will be calculated based on the actual weight and the final solution volume. These factors will be put into the instrument's procedure and a final concentration of metal in solid will be reported on a ng metal /g solid basis.

APPENDIX A

STANDARD OPERATING PROCEDURE

WEIGHING WIPE SAMPLE FILTER MEDIA

A. Balance Operation

1. There are a few fundamental rules that should be followed when using the Cahn C-30 microbalance.
   a. Always use forceps to handle objects to be weighed.
   b. Always apply the brake when placing an object on or removing an object from the stirrup.
   c. Always pass both sides of the object to be weighed in front of a deionizer to eliminate static electricity.
   d. Always make sure that the door is closed and the brake is released when weighing an object or taring the balance.
   e. Always let the balance stabilize before taking a reading. A reading should remain stable for at least fifteen seconds before you record it.
2. After the power is initially turned on, the Cahn C-30 microbalance must be warmed up for at least **6 hours** before it can be used. Because of this the balance is usually left on continuously.

B. Balance Calibration

1. Use the RANGE button to select range A.
2. If the stirrups are not on the balance:
   a. Press the TARE button.
   b. Hook one stirrup onto the A loop and the other onto the TARE loop.
   c. The reading should be negative. If the reading is not negative, reverse the stirrups.
3. Press the TARE button.

4. Place the 200 mg calibration weight on the A stirrup. When the reading stabilizes press the CAL button.
5. Apply and then release the brake. Make sure the reading stabilizes at 200.000 ± 0.005 mg. If the reading does not stabilize at 200.00 mg, press the CAL button and repeat this step.
6. Remove the calibration weight from the balance.

C. Weighing Filters

NOTE: Do not use the balance if the temperature of the weighing room is not 18.1 ± 0.3 C or if the relative humidity exceeds 50%.

The blank filter media should be allowed to equilibrate to the weighing room conditions for a minimum of 24 hours prior to weighing. Filter media containing dust samples should be allowed to equilibrate for a minimum of 48 hours prior to weighing. This can be done by placing the filters in a dust-free chamber that is at the same temperature and humidity as the weighing room.

1. Remove stirrup A from the balance and rinse first with distilled-deionized water and then with methanol. When the stirrup is completely dry, replace it on the balance.
2. Calibrate the balance as outlined in section B. Record that the balance was calibrated in the filter media notebook.
3. Record your name, the date, the lot number of the filter media to be weighed, and the temperature and relative humidity of the weighing room in the wipe sample notebook.
4. Zero the balance before each weighing.
5. For each dust sample to be weighed, place a 50 cm diameter weighing paper circle on stirrup A and zero the balance. This step is not necessary for blank filter media.
6. Weigh the filters as sets, three at a time, using the rules outlined in section A-1.
7. Record the I.D. number and the weight of each filter set in the log book.
8. Place the filter set in a clean in the envelope.
9. Affix a label with the filter ID code to the aluminum foil.

10. Place the filter set in a zip-lok bag.
11. Complete the sample identification and pre sampling sections of a wipe sample chain of custody (COC) form.
12. Fold the COC form and place it in the bag with the filter set.
13. Seal the bag.
14. Remove the weighing paper from stirrup A.
15. Recalibrate the balance after every 20 filter sets and note the calibration in the wipe sample notebook.
16. Store the filter sets in a cool dry place until they are to be used.

APPENDIX B

STANDARD OPERATING PROCEDURE

WEIGHING SOIL SAMPLES

Soil sample will be weighed on a Sartorius A120S Balance.

1. Clear any debris from the pan or weighing chamber of the balance.
2. Close all glass doors on the balance.
3. Turn on the balance by pressing the ON/OFF button.
4. Press the TARE button to zero the balance.
5. Press the CAL button to calibrate the balance. After the balance beeps it will be ready for use.
6. Open one of the side doors of the balance and place a clean weighing boat on the pan.
7. Close the balance door and press the TARE button to zero the balance.
8. Record your name and the date in the vacuum sample data sheet.
9. Open the side door of the balance and remove the boat.
10. Place the plastic soil sample bag in the boat and weight the bag and boat.
11. Remove the bag and boat from the balance.
12. Scrape bag if necessary with a teflon coated spatula, to remove all of the soil possible, on to the boat.
13. Homogenize the particles in the boat with a teflon coated spatula
14. Return the boat to the balance, close the balance door and record the weight of the soil.
15. Open balance door and remove the boat.
16. In the notebook, record the soil sample collection bag ID code and the weights.
17. Place a microwave digestion tube on the pan and repeat steps 6 and 7 for the tube.
18. Remove the tube from the balance and using a teflon coated spatula transfer about 0.5 g of soil to digestion vessel.

19. Return the tube to the balance and record the soil weight in the lab notebook.
20. Return the bag and remaining soil to the sample storage bag seal the bag and save for sub sample removal and shipment to RTI for As analysis.
21. Complete the chain of custody form.
22. Fold the chain of custody form, place it with the sample storage bag, and seal the bag.
23. If samples are being weighed then place a new weighing boat on the pan.
24. Close the balance door and press the TARE button to zero the balance.
25. Repeat steps 9 through 23 for each sample to be weighed.