

National Human Exposure Assessment Survey (NHEXAS)

Arizona Study

Quality Systems and Implementation Plan for Human Exposure Assessment

The University of Arizona
Tucson, Arizona 85721

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Standard Operating Procedure

SOP-BCO-L-3.1

Title: Extraction of Metals from Soils Dust Air Filter and Surface and Dermal Wipe Samples for AA (Graphite Furnace or Flame) or ICP-AES Analysis

Source: The University of Arizona

U.S. Environmental Protection Agency
Office of Research and Development
Human Exposure & Atmospheric Sciences Division
Human Exposure Research Branch

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Extraction of Metals from Soil, Dust, Air Filter, and Surface and Dermal Wipe Samples for AA (Graphite Furnace or Flame) or ICP-AES Analysis

1.0 Purpose and Applicability

This standard operating procedure (SOP) describes the acid digestion of soil, house dust, air filter, and surface or dermal wipe samples for analysis using inductively coupled plasma atomic emission spectroscopy (ICP-AES), and/or graphite furnace or flame atomic absorption spectroscopy (GFAA or FAA).

2.0 Definitions

- 2.1 Method Blank: all reagents (and a blank filter or wipe when appropriate) carried through the same digestion procedure as the samples, including filtration and any subsequent dilution.
- 2.2 Field Blanks: a blank filter or wipe, unwrapped in the field but not used for any sampling, carried through the same digestion procedure as the samples. Field blanks will be reported as actual samples.
- 2.3 Calibration Blank: a volume of ASTM Type I water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the instrument.
- 2.4 Initial Calibration Verification (ICV): standard used to determine whether an instrument is calibrated to within a preset limit ($\pm 15\%$).

3.0 References

- 3.1 Method 3050: "Acid Digestion of Sediments, Sludges, and Soils," Test Methods For Evaluating Solid Waste, Volume 1A: Laboratory Manual - Physical/Chemical Methods, US EPA, Office of Solid Waste and Emergency Response, Washington, DC, SW-846, 3rd Edition, November 1986.
- 3.2 "Analytical Methods for the Determination of Inorganic Compounds Collected on Hi-Vol Filters and Analyzed by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Graphite Furnace Atomic Absorption (GFAA) Spectrometry," Exhibit D, US EPA Contract Laboratory Program Statement of Work for Analysis of Ambient Air (AA), Rev. IAIR01.2, October 1993.

- 3.3 "Standard Practice for Measurement of Metals in Workplace Atmosphere by Atomic Absorption Spectrophotometry," ASTM D 4185, Annual Book of ASTM Standards, Vol. 11.03, 1990.
- 3.4 "Standard Practice for Nitric Acid Digestion of Solid Waste," ASTM D 5198, Annual Book of ASTM Standards, Vol. 11.04, 1992.
- 3.5 "Standard Practice for Total Digestion of Sediment Samples for Chemical Analysis of Various Metals," ASTM D 4698, Annual Book of ASTM Standards, Vol. 11.02, 1992.
- 3.6 "Standard Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals," ASTM E 50, Annual Book of ASTM Standards, Vol. 3.05, 1990.
- 3.7 "Standard Specification for Reagent Water," ASTM D 1193, Annual Book of ASTM Standards, Vol. 11.01, 11.03, 1991.

4.0 Discussion

- 4.1 This method is an acid digestion procedure for determining the soluble metals content of soil, house dust, air filter, and surface or dermal wipe samples. Resulting sample digestates are intended for analysis using GFAA, FAA, and/or ICP-AES.
 - 4.1.1 A representative sample is digested in nitric acid and hydrogen peroxide.
 - 4.1.2 The digestate is then refluxed with either nitric acid or hydrochloric acid.
 - 4.1.3 Dilute hydrochloric acid is used as the final reflux acid for:
 - (1) the hydride AAS of As
 - (2) the ICP or FAA analysis of Ba, Cd, Cr, Cu, Mn, Ni, Pb, Se, V, and Zn.
 - 4.1.4 Dilute nitric acid is used as the final dilution acid for the GFAA analysis of As, Cd, Cr, Pb, Se, and V.
 - 4.1.5 The digestate is diluted to a final volume of 100 mL.

5.0 Responsibilities

- 5.1 The sample extractions will be performed by staff of the Atmospheric Sciences and Applied Technology Department at Battelle who are working on the NHEXAS program.
- 5.2 These staff will be responsible for obtaining samples from the sample coordinator, entering relevant information in the extraction/prep log books, sending final extracts for analyses, and filing analyte concentration values with the database coordinator.

6.0 Materials and Reagents

6.1 Materials

- 6.1.1 Pyrex beakers, 100 mL and 250 mL.
- 6.1.2 Watch glasses.
- 6.1.3 Gravity convection drying oven, ~5 ft³, 30 - 120 °C range.
- 6.1.4 Thermometer, 0 - 200°C range.
- 6.1.5 Filter paper, Whatman #41 (quantitative), or syringe filters (or equivalent).
- 6.1.6 Glass funnels, Pyrex 60° (or equivalent), with a 6-in stem length.
- 6.1.7 Volumetric flasks, Pyrex, class A, 100 mL, stoppered.
- 6.1.8 Pipettes and pipette tips, Eppendorf calibrated (or equivalent), fixed or adjustable volume, 5 - 10,000 µL.
- 6.1.9 Analytical balance, Mettler AE160 (or equivalent), capable of weighing to 0.01 g.
- 6.1.10 Fume hood.
- 6.1.11 Hot plate, Sybron/Thermolyne (or equivalent), 30-120 °C range.

6.2 Reagents

- 6.2.1 Concentrated nitric acid (HNO_3), trace metals analysis grade, or equivalent.
- 6.2.2 Concentrated hydrochloric acid (HCl), trace metals analysis grade or equivalent.
- 6.2.3 Hydrogen peroxide (H_2O_2), 30%, ACS reagent grade or equivalent.
- 6.2.4 ASTM Type II water (ASTM D 1193).

7.0 Procedure

7.1 Sample Extraction

- 7.1.1 All sample containers must be prewashed according to SOP BCO-L-10.0, with the exception of polyethylene zip-seal bags.
- 7.1.2 Remove excess hair and other foreign material from dust samples that have been sieved previously as per SOP UA-L-11.0. Mix soil or dust sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 0.50 to 2.00 g portion of sample to a 100 mL glass beaker. Record the sample ID and sample weight in the NHEXAS inorganic laboratory record book. Filter samples should be received folded in half, with the side containing the particulate folded into itself, in a polyethylene zip-seal bag. Transfer the entire filter or wipe to the beaker and record its weight.
- 7.1.3 Add 10 mL of 1:1 HNO_3 , or enough to cover the sample. Record the volume in the project inorganic laboratory record book. Swirl the solution to mix or coat sample with acid solution, and cover with a watch glass.
- 7.1.4 Heat the sample to ca 95°C and reflux for 10 to 15 min, or until only 5 mL of sample solution remains, without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3 , replace the watch glass, and reflux for 30 min. NOTE: Use caution when working with concentrated nitric acid. Add the nitric acid slowly, with gentle swirling, because nitric acid may react violently with some samples containing organic material.
- 7.1.5 Repeat this last step to ensure complete oxidation. Eclipse the watch glass and allow the solution to evaporate to 5 mL without boiling, while

maintaining a covering of solution over the bottom of the beaker. Do not permit the sample to evaporate to dryness.

- 7.1.6 After Steps 7.1.3-7.1.5 have been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H_2O_2 . Cover the beaker with a watch glass and return the covered beaker to the hot plate for gentle warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence caused by excess heat. Gently warm sample until effervescence subsides, and cool the beaker.
- 7.1.7 Continue to add 30% H_2O_2 in 1 mL aliquots with gentle warming until the effervescence is minimal, or until the general sample appearance is unchanged. **Do not add more than a total of 10 mL 30% H_2O_2 .**
- 7.1.8 If the sample is being prepared for: (1) hydride AAS of As, or (2) ICP or FAA analysis of Ba, Cd, Cr, Cu, Mn, Ni, Pb, Se, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling.
 - 7.1.8.1 After cooling, rinse watch glass and sides of beaker with Type II water. Decant extract with rinsing into a 100 mL volumetric flask.
 - 7.1.8.2 If there is any of the filter disk or wipe material left in the beaker, add Type II water to the 40 mL mark on the beaker, cover the beaker with a watch glass, set aside at room temperature for a minimum of 30 minutes. This is a critical step since it allows the acids trapped in the filter or wipe material to diffuse into the rinse water. If there is no filter or wipe material in the beaker, proceed to Step 7.1.8.3.
 - 7.1.8.3 Decant the solution into the volumetric flask, with rinsings until the volume in the flask appears to be ca 80-85 mL. Stopper the flask, shake vigorously, and set aside until any foam formed has dissipated. Particulates in the digestate that may clog the nebulizer of the analytical instrument should be removed by paper or gravity filtration. After filtration, dilute to the 100 mL mark with Type II water, stopper, and mix solution thoroughly.

- 7.1.8.4 The diluted sample contains 5% (v/v) HCl and 5% (v/v) HNO₃. Hence, instrument calibration solutions should be prepared in 5% (v/v) HCl, 5% (v/v) HNO₃.
- 7.1.9 If the sample is being prepared for GFAA analysis of As, Be, Cd, Co, Cr, Mo, Pb, Se, Tl, and V, then cover the sample with an eclipsed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to about 5 mL. Do not permit the sample to evaporate to dryness.
- 7.1.9.1 After cooling, rinse watch glass and sides of beaker with Type II water. Decant extract with rinsing into a 100 mL volumetric flask. Refer to Steps 7.1.8.2 and 7.1.8.3 for the dilution procedure.
- 7.1.9.2 The diluted sample contains about 5% (v/v) HNO₃. Hence, instrument calibration solutions should be prepared in 5% (v/v) HNO₃.
- 7.1.10 The sample is now ready for analysis by AA (graphite furnace or flame) or ICP-AES, and may be stored at room temperature while awaiting analysis. (Refer to SOPs BCO-L-5.0, BCO-L-6.0, BCO-L-7.0, and BCO-L-8.0.)

7.2 General Considerations

- 7.2.1 All samples must initially be run undiluted (i.e., final product of the sample preparation procedure). When an analyte concentration exceeds the calibrated or linear range (as appropriate), reanalysis of the analyte(s) is required after the appropriate dilution. All sample dilutions shall be made with deionized water (ASTM Type II) appropriately acidified to maintain acid content and strength.
- 7.2.2 Laboratory glassware to be used in metals analyses must be cleaned according to SOP BCO-L-10.0, "Procedure for Cleaning Glassware to be Used for Inorganic Elemental Analysis." Samples must be digested in a hood. Stock solutions to be used for preparing instrument or method calibration standards may be purchased and must be traceable to NIST, J.T. Baker, or equivalent.
- 7.2.3 Care must be taken to avoid losses through volatilization when using this extraction method for hydride-forming elements, such as arsenic and selenium. Spiked soil, dust, filters, and wipes, or appropriate NIST reference materials must be regularly digested alongside samples to ensure

adequate arsenic, selenium, and other target element recoveries (see Section 7.4).

7.3 Calculations

- 7.3.1 The relative percent difference (RPD) between duplicate digestions of the same sample is determined from:

$$RPD (\%) = \frac{(|C_1 - C_2|)}{0.5(C_1 + C_2)} \times 100$$

where C_1 = concentration of target element in digestion 1 of sample 1; and C_2 = concentration of target element in the duplicate digestion of sample 1.

- 7.3.2 The percent recovery of target elements in LSF spiked samples is expressed as:

$$\text{Recovery (\%)} = \left[\frac{\{ (C_{spk+sam})(V_{spk+sam}) / W_{spk} \} W_{samp} - (C_{samp} \cdot V_{samp})}{C_{spk} \cdot V_{spk}} \right] \cdot 100$$

where $C_{spk+sam}$ = concentration of target element in the spiked sample; $V_{spk+sam}$ = volume of the spiked sample; W_{spk} = weight of the spiked sample; W_{samp} = weight of the sample; C_{samp} = concentration of the target element in the sample; V_{samp} = volume of the sample; C_{spk} = concentration of the target element in the spike aliquot; V_{spk} = volume of the spike aliquot.

- 7.3.3 The percent recovery of target elements in NIST Standard Reference Materials is expressed as:

$$\text{Recovery (\%)} = \left(\frac{C_{meas}}{C_{cert}} \right) \times 100$$

where C_{meas} = concentration of the target element measured by analyst; C_{cert} = concentration of the target element certified by NIST.

7.4 Quality Control

- 7.4.1 Duplicate samples will be digested for soil and house dust at a rate of no fewer than one duplicate for every 20 samples digested. However, it is recommended that one duplicate sample be digested for every batch of samples digested simultaneously. RPDs will be calculated and reported.
- 7.4.2 Pre-digestion spiked samples or appropriate NIST SRMs will be digested at a rate of one per batch of samples simultaneously digested; and no fewer than one for every 20 samples digested. Percent recoveries will be calculated and reported. Any percent recoveries greater than 125% or less than 75% must be addressed by the Project Laboratory Director.
- 7.4.3 Method Blanks will be prepared at a rate of two per batch of samples simultaneously digested; and no fewer than one for every 10 samples digested. Reported sample results will reflect method blank corrections.
- 7.4.4 Field Blanks will be prepared and reported as samples in order to isolate possible contamination sources.
- 7.4.5 Automatic pipettes will be calibrated and maintained according to SOP BCO-L-9.0, "Operation, Calibration, and Maintenance of Fixed-Adjustable-Volume Pipette Guns."
- 7.4.6 Should any sample be evaporated to dryness, a new aliquot of dust/soil must be redigested. In the event that a second sample aliquot is not available (e.g., wipes, filters, and limited dust/soil samples), a notation that the sample was evaporated to dryness must be made in the laboratory notebook, and the sample results must be flagged.

8.0 Records

- 8.1 Records of all laboratory digestion procedures will be recorded in the study record book.
- 8.2 Records of pipette gun calibration will be recorded in the pipette gun record book.
- 8.3 Records of glassware acid bath maintenance will be recorded in the acid bath record book.
- 8.4 Electrical resistivity (megohms-cm, 25°C) of all Type II water stations will be recorded with daily use in the deionized water stations log books.