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## Acid Digestion of Flame Retardant Samples for Analysis by ICP-AES

### 1. SCOPE AND APPLICABILITY

This standard operating procedure (SOP) is used to digest solid samples containing flame retardants such as polyurethane foam, cover fabric, foam pad, synthetic fiber pad, synthetic fiber batting, synthetic beads, and plumage samples. This SOP is designed for total digestion for most samples. The procedure utilizes strong acids at elevated temperature to dissolve most elements.

This SOP has been developed to provide the digestion procedure for analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). All of the digested samples are analyzed by ICP-AES or ICP-MS to determine the following total metals.

Aluminum (Al)	Antimony (Sb)	Calcium (Ca)	Iron (Fe)
Magnesium (Mg)	Phosphorus (P)		

### 2. PRINCIPLE

Acid digestion is performed to dissolve metals in solid samples into acid solution because metals cannot be dissolved in water or organic solvents. To digest a solid sample matrix, combinations of acids along with elevated temperature are used. Nitric acid (HNO<sub>3</sub>) is an oxidizing acid used to decompose organic sample materials by breaking down complex hydrocarbons into water and carbon dioxide and to oxidize metals by forming soluble metal nitrates. The digestate solutions are analyzed by ICP-AES or ICP-MS to determine the concentration of metals or elements.

### 3. INTERFERENCES

#### 3.1. Contamination

Trace-level analysis requires careful and clean preparation and analysis technique along with high-purity standards and solutions. Solvents, reagents, glassware, and other items used during acid digestion may introduce unexpected interferences or contamination to the sample prior to analysis. These materials must be demonstrated to be free from interferences and contamination by analyzing a method blank with every sample batch.

### 3.2. Other Interferences

Samples often contain different matrices that may present challenges during digestion and analysis. Other types of interferences such as matrix, physical, chemical, and spectral interferences are discussed in detail in the “Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Optical Emission Spectroscopy”, DCN: 03.6010.00, and “Determination of Phosphorus in Flame Retardant Samples by ICP-AES”, DCN: 03.6010.01.

## 4. PRESERVATION AND HOLDING TIMES

Keep samples in the packaging they arrived in and store at <6°C. Samples are stored in sealed glass jars or sealed plastic bags with the sample fully enclosed in aluminum foil. Long term storage should be at <6°C in the aforementioned containment vessels.

Cryomilled samples should be stored in sealed glass vials and in the dark at <6°C when not in use.

Samples must be digested within 6 months of the sampling date. Digestates of samples must be stored in a fume hood and analyzed within 6 months of the sampling date.

## 5. EQUIPMENT AND SETUP

- Carbon steel blade, Miltex 4-111 No. 11 or equivalent
- HotBlock, Environmental Express SC100 or equivalent
- 50-mL VersaTube flip-top digestion tube, Starplex Scientific VT502 or equivalent
- 50-mL Centrifuge tubes, Greiner Bio-One 210261 or equivalent
- Tongue depressor, 6-in, Puritan REF 704 or equivalent
- Filter paper, 125-mm diameter, Whatman # 541, 1541-125 or equivalent

*Note: Do not use FilterMate (2µm PTFE-faced polypropylene filter, Environmental Express SC0401) to filter the samples for phosphorus analysis. Studies have shown contamination/interference in method blanks when FilterMate was used to filter samples.*

- Disposable polypropylene funnels, 65-mm top I.D., VWR 414004-288 or equivalent
- 18-Place polycarbonate racks or equivalent
- 0.1-10 mL Electronic pipettor with disposable tips or equivalent
- Analytical balance, capable of weighing down to 0.0001g
- Thermometer, capable of measuring up to 100°C
- 125-mL Erlenmeyer flask or equivalent
- 250-mL Griffin beaker or equivalent
- 2-L Volumetric flask or equivalent
- 25-mL or 100-mL Volumetric flask, standard glass or equivalent

- Disposable nitrile gloves
- Plastic bags for solid waste

## 6. STANDARDS AND REAGENTS USED

### 6.1. Reagents

The reagents listed below are all reagent grade and explained further in Appendix A.

- Reagent water
- Concentrated nitric acid (HNO<sub>3</sub>)
- 5% HNO<sub>3</sub>

### 6.2. Standards

The standard listed below is explained further in Appendix A.

- 500 ppm Phosphorus and Antimony Spike Standard (P & Sb Spike 500)
- MDL Spike Standard (P & Sb LLQC)

## 7. METHOD PROCEDURE

### 7.1. Batch QC Requirements

The following Quality Control (QC) analyses must be performed for each digestion batch. A digestion batch is defined as up to 20 samples, excluding the QC samples prepared together within a 24 hour period. All of the QC samples must be carried through the complete digestion and analysis processes along with the samples. The details on QC criteria are provided in the SOP for EPA Method 6010C DCN:03.6010.00, Sec. 6.3 and Determination of Phosphorus in Flame Retardant Samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). All formulas and sample calculations are also listed in Appendix B in the SOP for EPA Method 6010C (DCN:03.6010.00).

#### 7.1.1. Method Blank (MB)

- A MB is used to monitor background contamination in the sample preparation process.
- A MB must be prepared as part of every digestion batch using reagent water matching the mass of the samples.

#### 7.1.2. Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD)

- A LCS and a LCSD are used to monitor the efficiency and accuracy of the digestion processes in a clean matrix.
- For each digestion batch, at least one LCS must be prepared by spiking 1.25 mL of P & Sb Spike 500 (See Appendix A) into reagent water

matching the mass of the samples. In cases where matrix spiking is not possible or unsuitable for the sample matrix or when an additional measure of accuracy and precision for the analysis is needed, a LCS may be used along with the normal LCS.

### 7.1.3. Method Detection Limit Sample (MDL)

- For every digestion batch, a Method Detection Limit Sample (MDL) or a Lower Level Quality Control Sample (LLQC) should be prepared by spiking 1.25 mL of MDL Spike Standard (P & Sb LLQC) (See Appendix A) into reagent water matching the mass of the samples.

### 7.1.4. Duplicate (Dup) or Triplicate (Tri) Samples

- Duplicate or triplicate samples are used to determine the homogeneity of the sample by calculating the precision of the analysis in samples known to contain analytes of interest. More frequent duplicate or triplicate samples should be prepared if the sample characteristics within the digestion batch appear to have significant variability based on visual observation.
- Duplicate or triplicate samples should be analyzed as part of every digestion batch.

### 7.1.5. Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

- A MS and a MSD are used to document any potential changes in precision and bias as a result of the method in a given matrix. More frequent matrix spikes should be prepared if the sample characteristics within the digestion batch appear to have significant variability based on visual observation.
- For each digestion batch, a MS and a MSD should be prepared by spiking 1.25 mL of P & Sb Spike 500 (See Appendix A) into a sample respectively. Typically, one sample is chosen in a digestion batch for the MS/MSD unless sample characteristics within the digestion batch contain multiple matrices. In that case of multiple matrices in the batch, one sample is chosen for the MS/MSD per matrix.

## 7.2. Instrument QC requirements

Refer to the “Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Optical Emission Spectroscopy”, DCN: 03.6010.00 Sec. 6.2 for detailed instrument QC requirements.

## 7.3. Sample Preparation

### 7.3.1. Preliminary Steps

- (1) Check out samples. Refer to “Environmental Sample Receipt, Handling and Shipping at the Berkeley Facility” DCN:02.0014.00.

- (2) Check calibration of the analytical balance in Room 171 or 182 using scale calibration weights. Refer to “Calibration and Monitoring of Balances and Precision Mass Standards”, DCN: 02.0049.00. Fill out the Balance Check Log Sheet (DCN: 07.0202.00).
- (3) Check calibration of an electronic pipettor with disposable tips. Refer to the “Calibration Check Procedure for Automatic Air Displacement Pipettes”, DCN: 02.0050.00. Fill out the Pipette Daily Volume Check Log Sheet (DCN: 07.0067.00).
- (4) Turn on the HotBlock and set the temperature such that a thermometer in a 50-mL digestion vessel with reagent water will read  $95 \pm 5^\circ\text{C}$ .

### 7.3.2. Sample Digestion

- (1) Prepare 50-mL digestion vessels for all samples including QC samples in an 18-place polycarbonate rack. Label each vessel with the sample number. Add batch number and date on at least MB and LCS tubes. Fill out the Acid Digestion for SB 1019 Flame Retardant Samples Log Book (DCN: 07.0083.00).
- (2) Cut each sample into a minimum of 750 mg, not to exceed 770 mg, using carbon steel blade and place in a 50-mL digestion vessel. Use a new disposable tongue depressor for each unique sample to transfer if necessary.

*Note: Use 750  $\mu\text{L}$  of reagent water for MB, LCS, LCSD and LLQC. Weigh a minimum of 750 mg, not to exceed 770 mg, of each chosen sample for duplicate or triplicate and MS/MSD.*

*Note: This digestion method was originally developed based on polyurethane foam. Thus, some flame retardant samples may require different mass depending on their densities. Use less than 750 mg of samples if the samples fill up more than half of the digestion vessel and write the notes in the comments section of the log sheet.*

- (3) Add 1.25 mL of spike standard (P & Sb Spike 500) to LCS/LCSD and MS/MSD. Add 1.25 mL of MDL spike standard (P & Sb LLQC) to LLQC.
- (4) Add 10 mL of concentrated  $\text{HNO}_3$  to each digestion vessel and cover the vessel with an attached cap slightly opened.

*Note: Some samples may react violently when  $\text{HNO}_3$  is added! Add acid slowly to avoid sample losses and to maintain safety.*

- (5) Place the rack with the digestion vessels in the HotBlock all at once and reflux up to 4 hours at  $95 \pm 5^\circ\text{C}$ .

**Note:** Gently shake the digestion vessels about every 20 minutes and check the sample volume to make sure the samples do not dry. If the samples boil, some volatile elements may be lost. If brown fumes are generated while the samples are refluxing in the HotBlock, indicating oxidation of the sample by  $\text{HNO}_3$ , continue to reflux until no brown fumes are given off by the sample indicating complete reaction with  $\text{HNO}_3$ .

- (6) While refluxing, fold a Whatman No. 541 filter paper into funnel filter configuration and place the folded filter into a disposable polypropylene funnel. Rinse the filtering unit with 5%  $\text{HNO}_3$  and allow rinsings to drain into a 125-mL Erlenmeyer flask. Place the rinsed filtering unit in each 50-mL centrifuge tube, which is standing in a rack.
- (7) After the samples have refluxed for 4 hours, remove the digestion vessels from the HotBlock and turn off the HotBlock. Cool the digestate to room temperature.
- (8) Filter the cooled digested samples using the filtering units and collect filtrates in the corresponding 50-mL centrifuge tubes. Transfer the digested samples onto the filter directly. Place the attached cap slightly opened on the emptied digestion vessel.
- (9) Wash the filter papers with reagent water by dispensing water on the top of the sample on the filter paper. Collect all of the filtrates in the corresponding centrifuge tubes.
- (10) Rinse the attached caps with reagent water and filter the whole content of the digestion vessels. Collect the filtrate into the corresponding centrifuge tubes.
- (11) Rinse the walls of the digestion vessels at least three times with reagent water, and then rinse the samples on the filters at least three times with reagent water. Use small quantities of water to make sure that the solution will not overflow the 50 mL final volume. Collect everything into the corresponding centrifuge tubes.
- (12) Bring the final volume to 50 mL with reagent water.

*Note: When less than 750 mg of sample was used in Section 7.3.2. (2), bring the final volume to 25 mL with reagent water.*

- (13) Cap the centrifuge tubes and shake well.
- (14) Record all the information for the digestion in the Acid Digestion for SB 1019 Flame Retardant Samples Log Sheet (DCN: 07.0083.00) and sign the log sheet. Make sure that the digestion log sheet has been reviewed by another analyst. Make a copy of the digestion log sheet and give it to the analyst who will be analyzing the samples.

- (15) Move the sample vessels into a fume hood labeled “To Be Analyzed” in Room 171. Samples are ready for ICP-AES analysis as outlined in the SOP for “Determination of Phosphorus in Flame Retardant Samples by ICP-AES”, DCN 03.6010.01.

#### 7.4. Data Analysis

This SOP addresses sample preparation only. For details on data analysis, including review of the QC required along with corrective actions required upon failure of the specific QC, refer to the Batch QC Requirements in Section 7.1 as well as the “Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Optical Emission Spectroscopy”, DCN: 03.6010.00 and “Determination of Phosphorus in Flame Retardant Samples by ICP-AES”, DCN 03.6010.01 for details.

#### 7.5. Data Reporting

Record all the information for the digestion in the Acid Digestion for SB 1019 Flame Retardant Samples Log Sheet (DCN: 07.0083.00) and sign the log sheet. Make sure that the digestion log sheet has been reviewed by another analyst. Make a copy of the digestion log sheet to be included in the final report package. Create a “Sample Preparation Report” in LIMS. Refer to “Quality System Procedure for Data Upload, Report Generation and Editing Using ECL LIMS” DCN: 02.0053.00. Print out the Sample Preparation Report and give it to an ICP -AES analyst. Make a copy of the Certificate of Analysis (COA) and the ICP-AES Standards Preparation Log Sheet (DCN: 07.0013.00) for all standards used as spiking solutions. Refer to the “Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Optical Emission Spectroscopy”, DCN: 03.6010.00 for details on how to retain COAs and the ICP-AES Standards Preparation Log Book (DCN: 07.0013.00).

#### 7.6. Method Performance

This digestion method was originally developed based on polyurethane foam samples. Analysts should carefully choose the appropriate mass of each sample depending on the density for flame retardant samples other than polyurethane foams.

### 8. MAINTENANCE AND TROUBLE SHOOTING

- The HotBlock requires no routine parts replacement. After each use, clean exterior surface with a damp sponge to remove acid residue. For acid spills, sponge with a diluted solution of sodium bicarbonate followed by distilled water. Acid that spilled directly into the digestion wells should be neutralized and removed. Avoid excessive spills, as liquid allowed to overflow into the HotBlock casing can seriously damage electric components.
- Dispose all used reagents, solutions, and samples properly. If any of the items are hazardous, dispose in a hazardous waste container. Refer to “Management and Disposal of Laboratory Generated Waste Berkeley Facility” DCN:09.0009.00 for details.
- Clean any spill or mess at and around work area.
- Replenish all supplies when necessary.

## 9. REFERENCES

- 9.1. "Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Optical Emission Spectroscopy", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.6010.00
- 9.2. "Determination of Phosphorus in Flame Retardant Samples by ICP-AES", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.6010.01
- 9.3. "Environmental Sample Receipt, Handling and Shipping at the Berkeley Facility", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN:02.0014.00
- 9.4. "Calibration and Monitoring of Balances and Precision Mass Standards", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 02.0049.00
- 9.5. "Balance Check Log Sheet", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 07.0202.00
- 9.6. "Calibration Check Procedure for Automatic Air Displacement Pipettes", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 02.0050.00
- 9.7. "Pipette Daily Volume Check Log Sheet", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 07.0067.00
- 9.8. "Acid Digestion for SB 1019 Flame Retardant Samples", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 07.0083.00
- 9.9. "Quality System Procedure for Data Upload, Report Generation and Editing Using ECL LIMS", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 02.0053.00
- 9.10. "ICP-AES Standards Preparation Log Sheet", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 07.0013.00
- 9.11. "Management and Disposal of Laboratory Generated Waste Berkeley Facility", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 09.0009.00

## APPENDIX A Current Reagents and Standards Used

### • REAGENTS

The reagents currently in use are as follows:

#### ○ Reagent water

All references to water in the SOP refer to reagent water, unless otherwise specified. Reagent water must be free of interferences. Use the reagent water from the Millipore Milli-Q.

#### ○ Concentrated nitric acid (HNO<sub>3</sub>)

- Ultrapure trace metal grade, or equivalent

#### ○ 5% HNO<sub>3</sub>

Dilute 100 mL of concentrated HNO<sub>3</sub> to a final volume of 2 L with reagent water in a 2-L volumetric flask and mix thoroughly.

### • STANDARDS

The standards currently in use are as follows:

#### ○ Stock Solutions

The stock solutions currently in use are as follows:

Name	Analytes
Phosphorus Stock	10000 ppm P
Antimony Stock	10000 ppm Sb

○ **500 ppm Phosphorus and Antimony Spike Standard (P & Sb Spike 500)**

- Prepare the 500 ppm phosphorus and antimony spike standard (P & Sb Spike 500) using stock solutions listed above.
- Rinse a 100-mL volumetric flask three times with 5% HNO<sub>3</sub> solution.
- Pipette 5 mL each of the 10000 ppm Phosphorus Stock and 10000 ppm Antimony Stock into the volumetric flask.
- Bring to volume with 5% HNO<sub>3</sub> solution and mix thoroughly.
- Fill out the ICP-AES Standards Preparation Log Book (DCN: 07.0013.00).
- This P & Sb Spike 500 standard calibration working standard will expire 6 months from the preparation date.

○ **MDL Spike Standard (P & Sb LLQC)**

- Pipette 1.8 mL of the P & Sb Spike 500 standard into a 100-mL volumetric flask. Bring to volume using 5% HNO<sub>3</sub> and mix thoroughly. This MDL spike solution (P & Sb LLQC) contains 9.0 ppm of P and Sb and will expire 6 months from the preparation date.

