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Determination of Phosphorus in Flame Retardant Samples by ICP-AES

1. SCOPE AND APPLICABILITY

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is a powerful tool for the analysis of trace elements; however, the sample must be in solution-form for analysis. As a result, all samples potentially containing flame retardant chemicals (FRS) must be digested using an appropriate acid-digestion method before analysis can occur. To the extent possible, standards and samples shall be matrix-matched. Prior to analysis, analysts shall review all preparation methods used to prepare samples for analysis to familiarize themselves with the relevant quality control procedures, development of QC acceptance criteria, calculations, and general guidance.

This standard operating procedure (SOP) is used to analyze FRS such as polyurethane foam, cover fabric, foam pad, synthetic fiber pad, synthetic fiber batting, synthetic beads, and plumage samples or similar. This SOP has been developed to quantify phosphorus (P) and antimony (Sb) concentrations by ICP-AES when FRS is digested using the "Acid Digestion of Flame Retardant Samples for Analysis by ICP-AES", DCN: 05.0033.00 or "Microwave Assisted Digestion", DCN: 03.3051.00 and "Technical SOP for Operation of Milestone UltraWAVE Microwave Digestion Unit", DCN: 03.3051.01. In this method, yttrium (Y) is selected as an internal standard and aluminum (Al), calcium (Ca), iron (Fe) and magnesium (Mg) are quantified in FRS because they are known to cause spectral interferences. Additional elements may be analyzed by this method if appropriate validation at the concentrations of interest is provided. Please refer to the "Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Optical Emission Spectroscopy", DCN: 03.6010.00 (SOP for EPA Method 6010C: ICP-OES) for more information. Appendix A describes how to screen (semi-quantify) elements listed in the SOP for EPA method 6010C: ICP-OES in FRS.

In this SOP, digestates of FRS are analyzed by the PerkinElmer Optima 7300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) or the Agilent SVDV 5100 ICP-OES. [Table 1](#) lists the elements for which this method has been validated as well as the analytical wavelengths, plasma views, and instrument detection limits (IDLs) in clean aqueous matrices without the presence of background interferences.

2. PRINCIPLE

For general information regarding principle, please refer to the SOP for EPA Method 6010C: ICP-OES, Section 2.

3. INTERFERENCES

For general information regarding interferences, please refer to the SOP for EPA Method 6010C: **ICP-OES**, Section 3.

Note: Although FilterMate (2µm PTFE-faced polypropylene filter, Environmental Express SC0401) is usually used to filter suspended solids in digestates before analysis using EPA Method 6010C at ECL, DO NOT use FilterMate to filter the samples for phosphorus analysis. Studies have shown contamination/interference in method blanks when FilterMate was used to filter samples. If filtration is required before analysis, use a Whatman No. 541 filter paper or a Waters Acrodisc syringe filter (PVDF 0.45 µm). Other equivalent filters can be used once studies show no contamination/interference in method blanks due to filtration.

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

Digestates of FRS are analyzed by the PerkinElmer Optima 7300 DV ICP-OES with Elemental Scientific FAST 2DX Autosampler or the Agilent SVDV 5100 ICP-OES with SPS4 Autosampler.

For general information regarding key hardware and consumables, please refer to the SOP for EPA Method 6010C: **ICP-OES** Section 5.1. Please also refer to the Technical SOP for Metals Analysis using Perkin-Elmer Optima 7300 ICP-OES (**DCN: 03.6010.02**) and the Technical SOP for Metals Analysis using Agilent SVDV 5100 ICP-OES (**DCN: 03.6010.03**).

The nebulizer used for FRS analysis represents the only departure from the SOP for EPA Method 6010C: **ICP-OES. PFA ST3-70 MicroFlow nebulizer (PerkinElmer) was** used to validate this method to analyze FRS. High dissolved solids nebulizers are for samples with high dissolved solids (up to 20%). A high dissolved solids nebulizer or an equivalent nebulizer should be used to analyze FRS.

6. STANDARDS AND REAGENTS USED

A complete list of all stock solutions as well as the procedure for the preparation of all solutions and standards can be found in **Appendix B**. All standard preparation shall be recorded in the "ICP-AES Standards Preparation **Log**" (**DCN: 07.0013.00**).

- Reagent Water
- Concentrated Nitric Acid (68-70% HNO₃)

- 2% (v/v) HNO₃ Instrument Rinse Solution
- 5% (v/v) HNO₃ for Mixing Standards
- Stock Solutions – See [Appendix B](#) for a list of all stock solutions

All stock solutions shall be purchased as a certified standard with both lot number and expiration date on the bottle. These solutions shall be labeled with the date they are received by the laboratory and with the date the solution was first opened.

- Calibration Blank (ICB/CCB)
- 500 ppm Phosphorus and Antimony Spike Standard (P & Sb Spike 500)
- 100 ppm Calibration Working Standard (P & Sb Cal 100)
- Instrument Calibration Standards

A description of the current calibration standards and ranges can be found in [Appendix B](#).

- 50 ppm Yttrium Internal Standard
- Second Source/Initial Calibration Verification Standard (P & Sb ICV 5)

The second source calibration verification standard should be prepared using a certified solution obtained from a different supplier than that used for calibration. If there is only one supplier for the desired analyte, the second source may be from a stock with a different lot number than the calibration stock solutions.

- Low-Level Calibration Verification (LLCV) and Continuing Calibration Verification (CCV) Solutions
- Interference Check/Inter-Element Correction Standard (P & Sb IEC)
- MDL Spike (P & Sb LLQC)
- X-Y Alignment Solutions – 1 ppm Mn (axial), 10 ppm (radial)

The source of these solutions may be the same as either the calibration stock or the second source stock or may be from a different source entirely. Because the X-Y alignment looks for the strongest signal as a set point and is not calibrating for a specific value, solutions must be from a certified source but may exceed the expiration date by 1 year before replacement is needed. Please refer to the SOP for EPA Method 6010C: [ICP-OES](#) Appendix A (Optimization Solutions) on how to prepare the solutions.

7. METHOD PROCEDURE

7.1. Instrument Validation

Please refer to the SOP for EPA Method 6010C: **ICP-OES** Section 6.1. Typical plasma conditions and pump settings are shown in [Table 2](#) for FRS analysis.

7.2. Instrument Operation (Instrument QC requirements)

Please refer to the SOP for EPA Method 6010C: **ICP-OES** Section 6.2.

7.3. Method-Based Quality Control Samples (Batch QC Requirements)

Please refer to the SOP for EPA Method 6010C: **ICP-OES** Section 6.3. The only different criteria to analyze FRS compared to the SOP for EPA Method 6010C: **ICP-OES** is a method blank. A method blank is considered acceptable if it does not contain target analytes at a concentration above the reporting limit or > 10 % of the lowest sample concentration for each analyte in a given batch, whichever concentration is higher. The current reporting limits of elements by ICP-AES analysis are 200 ppb for antimony, phosphorus, and iron and 500 ppb for aluminum, calcium, and magnesium.

A summary of the typical frequency of method-based quality control samples can be found in Table 3.

7.4. Sample Preparation

- Fill out all the sample preparation information in the ICP-AES Analytical Run Log (DCN: 07.0012.00).
- Prepare the samples for analysis, including any necessary dilutions and post digestion spikes.

Note: The standard protocol for FRS is to take 4 mL of digestate and bring the volume up to 10 mL with DI water before analysis when samples are digested by HotBlock using the SOP for "Acid Digestion of Flame Retardant Samples for Analysis by ICP-AES". Shake the sample vessel well and make sure that there is no bubble in the digestate. If there are bubbles, remove the bubbles by shaking the vessel again or transferring the digestate into another vessel. Digestates are run on ICP-AES *without* dilution when samples are digested by microwave using the SOP for "Microwave Assisted Digestion".

Note: Any sample which exceeds the linear calibration range must be diluted such that the concentration falls within the calibration range. Currently, P, Sb, and Fe are calibrated from 0.1 to 100 ppm and Al, Ca, and Mg are calibrated from 0.25 to 250 ppm.

- Place the prepared samples in the auto-sampler rack.

7.5. Data Analysis

QC Analysis worksheets are available to check whether the QC criteria are met.

- QC Analysis worksheets can be found in the templates directory on the L:\ drive at L:\Analytical Results\Inorganic Results\ICP Metals\Totals\Report Templates\ICP 7300 P and Sb QCCHECK
- Enter all raw data into the appropriate QC Analysis worksheet.
- Enter the sample IDs and raw data into the [Raw Data] tab.
- Enter the sample mass and dilution information into the [Samples] tab.
- Modify the template as needed.
- Import data into LIMS to generate a report and compare calculated values to those obtained in the QC Analysis worksheet.

7.6. Data Reporting

Please refer to the SOP for EPA Method 6010C: ICP-OES Section 6.4.

8. MAINTENANCE AND TROUBLE SHOOTING

For general information regarding maintenance and troubleshooting, please refer to the SOP for EPA Method 6010C: ICP-OES Section 7 and Appendix D.

9. REFERENCES

- (1) "Acid Digestion of Flame Retardant Samples for Analysis by ICP-AES", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 05.0033.00
- (2) "Microwave Assisted Digestion", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.3051.00
- (3) "Technical SOP for Operation of Milestone UltraWAVE Microwave Digestion Unit", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.3051.01.
- (4) "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
- (5) "Technical SOP for Metals Analysis using Perkin-Elmer Optima 7300 ICP-OES", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.6010.02
- (6) "Technical SOP for Metals Analysis using Agilent SVDV 5100 ICP-OES", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 03.6010.03

- (7) "ICP-AES Standards Preparation Log", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 07.0013.00
- (8) "ICP-AES Analytical Run Log", State of California Department of Toxic Substances Control, Environmental Chemistry Laboratory, DCN: 07.0012.00
- (9) Syngistix for ICP Software Guide

10. TABLES

Table 1: Analytical Wavelengths and Instrument Detection Limits

Analyte	Wavelength (nm)	Plasma View	IDL (ppm)*	Analyte	Wavelength (nm)	Plasma View	IDL (ppm)*
Phosphorus	214.9	Radial	0.0229	Antimony	206.8	Radial	0.0150

Note: * IDLs were determined using data on February 3rd, 5th, and 7th 2020 and are meant to be representative of typical IDLs for Optima 7300. Current IDLs may differ.

Table 2: Typical Plasma Conditions and Pump Settings

Argon Gas		Plasma	
Flow Rate	15 L/min	RF Power	1300 watts
Auxiliary	0.2 L/min	View Distance	15 mm
Nebulizer	0.60 L/min	Aerosol Type	Wet
		Source Equilibration Delay	15 sec
Pump		Spectrometer	
Pump Rate	2.0 mL/min	Read Delay	15 sec
Sample	2.0 mL/min	Number of Reads	3
Rinse	1.5 mL/min	Background Correction	2-Point

Table 3: Instrument and Method Quality Control Sample Frequency and Acceptance Criteria

QC Sample	Frequency	Acceptance Criteria
Instrument Quality Control		
Calibration Curve	Before Analysis	$R \geq 0.998$
Internal Standard Recovery	Every Sample	$\pm 30\%$ of Internal Standard in Calibration Blank
Initial Calibration Verification (ICV)	Before Analysis	$\pm 10\%$
Calibration Blank Verification (ICB/CCB)	Before Analysis; Every 10 samples; After Analysis	$\leq 25\%$ of RL
Low-Level Calibration Verification (LLCV)	Before Analysis; Every 10 samples; After Analysis	$\pm 30\%$
Continuing Calibration Verification (CCV)	Every 10 samples; After Analysis	$\pm 10\%$
Inter-Element Correction Verification (IEC)	Before Analysis	$\pm 20\%$
Batch Quality Control		
Method Blank (MB)	One per 20 sample batch	\leq RL or $\leq 10\%$ of lowest sample concentration
Laboratory Control Sample (LCS/LCSD)	One per 20 sample batch	$\pm 20\%$ recovery, $\leq 20\%$ RPD
Matrix Spike (MS/MSD)	One per 20 sample batch	$\pm 25\%$ recovery, $\leq 20\%$ RPD
Duplicate Sample (DUP)	One per 20 sample batch	$\leq 20\%$ RPD
Triplicate Sample (TRI)	One per 20 sample batch	$\leq 20\%$ RSD
Post Digestion Spike (PS)	If MS/MSD does not pass	$\pm 20\%$ recovery
Serial Dilution (SD)	If PS does not pass	$\pm 10\%$ RPD

11. APPENDICIES

Appendix A: How to Reprocess Data

Valuable data may be obtained by screening elements other than P, Sb, Al, Ca, Fe, and Mg. This section provides how to screen (semi-quantify) elements listed in the SOP for EPA method 6010C: **ICP-OES** in FRS using Syngistix for ICP software.

How to Add the Universal Data Acquisition Function

- To add the Universal Data Acquisition function to an existing method, click the **<Open>** icon in the “Method” ribbon under the “Analysis” menu in the main Syngistix for ICP window. In the Open Method window, select a method file (the most recent method created to analyze FRS using this SOP) to edit the method and click **<OK>**.
- In the main Syngistix for ICP window, click the **<Method>** icon to edit the method.
- In the Method Editor window, click the **<Options>** tab. Select the “Universal Data Acquisition” option under the “Save with Results” section. Select “Radial” or “Axial” depending on the needs.
- Save the method by clicking on **<Save>** icon in the “Method” ribbon under the “Analysis” menu in the main Syngistix for ICP window.
- Please refer to the Syngistix for ICP Software Guide for more details.

How to Process Data by Recalling Calibration

- In the main Syngistix for ICP window, click the **<Open>** icon in the “Method” ribbon under the “Analysis” menu. In the Open Method window, select a method file (the most recent method created to analyze Total Metals and WET Metals samples using the SOP for EPA method 6010C: **ICP-OES**) to reprocess the data and click **<OK>**.
- Recall the most recent calibration (which is used to analyze Total Metals or WET Metals samples using the SOP for EPA method 6010C: **ICP-OES**) by clicking on **<Recall Calibration>** under the “Calibration” ribbon under the “Results” menu. In the Select Results Data Set window, select a data set and click **<OK>**.
- In the main Syngistix for ICP window, click the **<Reprocess>** icon to reprocess data.
- In the Data Reprocessing window, click the **<Browse>** button for “Data set to preprocess”. In the Select Results Data Set window, select a FRS data set which requires reprocessing data and click **<OK>**. Highlight the specific samples which require reprocessing data by clicking each sample.
- In the Data Reprocessing window, click the “Save reprocessed data” option.

- In the Data Reprocessing window, click the <**Browse**> button for “Save reprocessed data to”. In the Select Results Data Set window, type “Name” and “Description” to be able to recognize the FRS data set after reprocessing by recalling a calibration and click <**OK**>.
- In the Data Reprocessing window, click the <**Reprocess**> button.
- In the main Syngistix for ICP, click the <**Results**> icon and print out the results.
- Please refer to the Syngistix for ICP Software Guide for more details.

Appendix B: Verification Levels and Solution Preparation for ICP-AES Analyses

Calibration Verification Levels

Instrument-Based QC Samples	Concentrations
Initial Calibration Verification (ICV)	5 ppm P and Sb
Continuing Calibration Verification (CCV)	5 ppm P, Sb, and Fe; 12.5 ppm Al, Ca, and Mg
Low-Level Calibration Verification (LLCV)	0.2 ppm P, Sb, and Fe; 0.5 ppm Al, Ca, and Mg
Inter-Element Correction Verification (IEC)	1 ppm P and Sb; 200 ppm Fe; 500 ppm Al, Ca, and Mg

Note: These instrument-based QC samples are currently used to verify the calibration during analysis and these concentration levels are current as of revision date.

Current Spiking Levels

Method-Based QC Samples	HotBlock Method (DCN: 05.0033.00)	Microwave Method (DCN: 03.3051.01)
Laboratory Control Sample (LCS/LCSD) in digestate	12.5 ppm P and Sb	5 ppm P and Sb
Laboratory Control Sample (LCS/LCSD) on ICP-AES	5 ppm P and Sb	5 ppm P and Sb
Matrix Spike (MS/MSD) in digestate	12.5 ppm P and Sb	5 ppm P and Sb
Matrix Spike (MS/MSD) on ICP-AES	5 ppm P and Sb	5 ppm P and Sb
Post Digestion Spike (PS)	5 ppm P and Sb	5 ppm P and Sb
MDL Spike (P & Sb LLQC) in digestate	0.225 ppm P and Sb	0.09 ppm P and Sb
MDL Spike (P & Sb LLQC) on ICP-AES	0.09 ppm P and Sb	0.09 ppm P and Sb

Note: These concentrations are currently used for the method-based QC samples as of revision date.

Stock Solutions

Name	Analytes
Phosphorus Stock	10000 ppm P
Phosphorus Second Source Stock	1000 ppm P
Antimony Stock	10000 ppm Sb
Antimony Second Source Stock	1000 ppm Sb
Majors Stock	2000 ppm Fe; 5000 ppm Al, Ca, Mg

Note: The stock solutions are currently in use and these concentration levels are current as of revision date.

Solutions for Rinsing and Dilution

Please refer to the SOP for EPA Method 6010C: **ICP-OES** Appendix A for the following rinsing and dilution solutions.

- **Reagent Water**
- **Concentrated Nitric Acid (HNO₃)**
- **2% (v/v) HNO₃ Instrument Rinse Solution**
- **5% (v/v) HNO₃ for Mixing Standards**

All subsequent uses of the term “5% HNO₃” refer to this solution. Please refer to the SOP for EPA Method 6010C: **ICP-OES** Appendix A “5% (v/v) HNO₃ Solution for Standard and Sample Dilutions”

Calibration Standards

- **Calibration Blank (ICB/CCB)**

The calibration blank shall be an aliquot of the same 5% HNO₃ solution used for the preparation of all standards.

- **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 **at least** three times with 5 % HNO₃ 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 % HNO₃ solution and mix thoroughly. Fill out the ICP-AES Standards Preparation **Log (DCN: 07.0013.00)**. This P & Sb Spike 500 contains 500 ppm of P and Sb and will expire **6 months** from the preparation date.

*Note: The spike standard **should** be validated by the Second Source/Initial Calibration Verification Standard (P & Sb ICV 5) prior to use in sample preparation.*

*Note: The expiration date can be extended beyond **6 months** once a study confirms that the standard concentration does not deviate from the initial concentration for prolonged storage. This is the same for other standards described below.*

Note: Rinse volumetric flasks with the same procedure and fill out the ICP-AES Standards Preparation Log Book to prepare for other standards described below.

- **100 ppm Calibration Working Standard (P & Sb Cal 100)**

To prepare the 100 ppm calibration working standard (P & Sb Cal 100), pipette 20 mL of the P & Sb Spike 500 standard and 5 mL of the Majors Stock into a 100-mL volumetric flask. Bring to volume using 5% HNO₃ solution and mix thoroughly. This P & Sb Cal 100

standard contains 100 ppm of P, Sb, and Fe and 250 ppm of Al, Ca, and Mg and will expire **6 months** from the preparation date.

- Instrument Calibration Standards**

A series of calibration standards at 0.1, 0.2, 0.5, 1, 5, 20, 50, and 100 ppm of P, Sb, and Fe (Concentration of Al, Ca, and Mg is 2.5 times higher than P, Sb, and Fe) shall be prepared in a volumetric flask as follows:

Calibration Standard (ppm)	Standards Used	Final Volume (mL)	Expiration
0.1	0.100 mL of P & Sb Cal 100	100	30 days
0.2	0.200 mL of P & Sb Cal 100	100	30 days
0.5	0.500 mL of P & Sb Cal 100	100	3 months
1.0	1.00 mL of P & Sb Cal 100	100	6 months
5.0	5.00 mL of P & Sb Cal 100	100	6 months
20	10.0 mL of P & Sb Cal 100	100	6 months
50	10.0 mL of P & Sb Spike 500; 2.50 mL of Majors Stock	100	6 months
100	20.0 mL of P & Sb Spike 500; 5.00 mL of Majors Stock	100	6 months

Bring the standards to volume using 5% HNO₃ solution. Standards may be made to final concentrations and/or volumes other than those shown above as needed. **These standards will expire from the preparation date as listed in the table above.**

Calibration Verification and Spike Solutions

- 50 ppm Yttrium Internal Standard**

Please refer to the SOP for EPA Method 6010C: **ICP-OES** Appendix A.

- Second Source/Initial Calibration Verification Standard (P & Sb ICV 5)**

Dilute 0.5 mL of the 1000 ppm Phosphorus Second Source Stock and the 1000 ppm Antimony Second Source Stock to a final volume of 100 mL using 5% HNO₃ solution in a 100-mL volumetric flask. Mix thoroughly. This P & Sb ICV 5 standard contains 5.0 ppm of P and Sb and will expire **6 months** from the preparation date.

- Low-Level Calibration Verification and Continuing Calibration Verification Solutions**

The LLCV and CCV solutions are the same as the calibration standards with corresponding concentrations.

Note: Currently, 0.2 ppm standard is used for the LLCV and 5.0 ppm standard is used for CCV.

- **Interference Check/Inter-Element Correction Standard (P & Sb IEC)**

Pipette 10 mL of the Majors Stock and 0.2 mL of the P & Sb Spike 500 standard into a 100-mL volumetric flask. Bring to volume using 5% HNO₃ and mix thoroughly. This P & Sb IEC standard contains 1.0 ppm of P and Sb, 200 ppm of Fe, and 500 ppm of Al, Ca, and Mg and will expire **6 months** from the preparation date.

- **MDL Spike (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% HNO₃ 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.

12. REVIEW

Signatures

Date
