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Status: Final

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Standard Operating Procedure for Determination of Phosphorus in Flame Retardant Samples by Inductively Coupled Plasma-Atomic Emission Spectroscopy

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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 flame retardant samples 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 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 has been developed to quantify phosphorus (P) and antimony (Sb) concentrations by ICP-AES when flame retardant samples are digested using the SOP for Acid Digestion of Flame Retardant Samples. In this method, yttrium (Y) is selected as an internal standard and aluminum (Al), calcium (Ca), iron (Fe) and magnesium (Mg) are quantified in flame retardant samples 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-Atomic Emission Spectroscopy (SOP for EPA Method 6010C: ICP-AES) for more information. Appendix A describes how to screen (semi-quantify) elements listed in the SOP for EPA method 6010: ICP-AES in flame retardant samples.

In this SOP, digestates of flame retardant samples are analyzed by the PerkinElmer Optima 7300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) equipped with demountable quartz torch, alumina injector, Gem Cone nebulizer, and cyclonic spray chamber. Data acquisition and processing are performed using PerkinElmer WinLab32 software. 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. Further information on the current instrument settings, standard concentrations, and expected concentrations of instrument and batch quality control samples may be found in Appendix B.

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2. PRINCIPLE

ICP-AES works by exciting the electrons in the analyte to an elevated state using RF-induced argon plasma. The excited electrons then collapse back to their ground state, emitting light at one of a fixed set of wavelengths characteristic to the specific analyte, often referred to as spectral lines. The instrument then measures the intensity of light emitted at specific spectral lines (as designated by the instrument operator), allowing for the simultaneous analysis of a wide range of analytes.

Due to variations in background radiation and scattering, background correction is essential for accurate trace element determination. To do so, background emission is measured adjacent to spectral lines for each analyte during analysis. The positions selected for the background-intensity measurement, which may be on either or both sides of the analytical line, are determined during method development based on the complexity of the spectrum adjacent to the spectral line. Ideally, the positions used should be as free as possible from spectral interference and should undergo the same change in background intensity as at the analyte wavelength measured during sample analysis. There is a possibility of interferences with the background correction; these can be monitored using method blank and laboratory control spike samples as described in Section 7.3.

3. SAFETY

Assume that all internal parts and pump tubing have been in contact with or contain acidic and/or toxic and potentially hazardous chemicals. Lab coat, gloves and safety glasses shall be worn when working with internal parts or changing pump tubing; change lab gloves frequently when working with internal parts to avoid contamination.

Concentrated nitric acid is moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.

Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

4. INTERFERENCES

For general information regarding interferences, please refer to the SOP for EPA Method 6010C: ICP-AES Section 4.

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.

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5. PRESERVATION AND HOLDING TIMES

Plastic bags and aluminum foils are both suitable for storage of samples. Samples may be stored at room temperature upon receipt. 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.

6. EQUIPMENT AND REAGENTS

6.1. Key Hardware and Consumables

For general information regarding key hardware and consumables, please refer to the SOP for EPA Method 6010C: ICP-AES Section 6.1. A list of the common consumables along with part numbers can be found in the SOP for EPA Method 6010C: ICP-AES Appendix C. A full list of the parts and consumables associated with the ICP-AES instrumentation may be found at L:\Supply_List.xls.

The only different part used to analyze flame retardant samples compared to the SOP for EPA Method 6010C: ICP-AES is the nebulizer. Instead of using a Meinhard Nebulizer Type C, a GemCone high dissolved solids nebulizer (PerkinElmer, Product number N0690670) was used to validate this method to analyze flame retardant samples. High solids GemCone nebulizers are for samples with high dissolved solids (up to 20%). This nebulizer allows analyzing samples with higher solid concentrations than is possible with a Meinhard nebulizer.

Note: The product number is current and available as of June 23, 2015.

6.2. Reagents and Standards

A complete list of all stock solutions with current supplier and part number 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 Book" (See Figure 1).

- Reagent Water
- Concentrated Nitric Acid (68-70% HNO_3)
- 2% (v/v) HNO_3 in Reagent Water as Instrument Rinse Solution
- 5% (v/v) HNO_3 in Reagent Water 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)

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- 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)
- 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-AES Appendix A (Optimization Solutions) on how to prepare the solutions.

7. METHOD PROCEDURE

7.1. Instrument Validation

Before using this procedure to analyze samples, the following data should be documented as the initial demonstration of performance. The linear dynamic range, instrumental detection limit, method detection limits and interference corrections need to be established for each individual target analyte on each particular instrument. These data shall be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. Any new wavelength or analyte added to the method must be validated before analysis at that wavelength may commence.

A hardcopy of all of the validation data shall be kept in a binder at ECL and be available for review. Any modifications shall be updated in the binder at the time of change. Additionally, past methods, IEC models, and detection limit development data will be stored in digital format on media separate from the computer associated with the instrument, when practicable.

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7.1.1. Instrument Method Parameters

The instrument method parameters are defined within the WinLab program and may vary slightly over time. This includes (but is not limited to) background correction locations, spectral lines used, lens settings, RF and gas flow settings and pumping rates. Typical spectral lines used for analysis along with the lens setting (axial or radial) are shown in Table 1. Typical plasma conditions and pump settings are show in Table 2.

Any time the instrument method is revised, the revision date must be included in the name of the method file when saved. This is essential to allow the connection of instrumental methods with past data sets, enabling re-examination of sample data if necessary.

7.1.2. Linear Dynamic Range

The linear dynamic range must be established for each analyte at each specific wavelength utilized under the same operating conditions as routine sample analysis by determining the signal responses across a wide range of sample concentrations. To do this, analyze a series of standards with increasing concentrations and plot the measured intensity (not measured concentration) as a function of theoretical concentration. The linear dynamic range is the range over which there is a linear relationship between concentration and signal intensity.

This process must be completed as part of the initial demonstration of performance and repeated annually or whenever a modification to the instrument results in a significant change in signal response (such as repair or replacement of detector components).

7.1.3. Calibration Range

Any range of calibration standards used for analysis of samples must be entirely within the determined linear dynamic range for that specific instrument and analyte. A minimum of a calibration blank and three non-zero standards must be used to define the calibration range, with the lowest standard defined as the lower limit of quantitation (LOQ), often referred to as the reporting limit.

Both a simple linear regression and a linear regression forced through zero are acceptable for the calculation of the best fit curve in the calibration as long as the resulting calibration meets all acceptance criteria and can be verified by acceptable QC results. Forcing the regression through zero cannot be used as a rationale for reporting results below the lowest standard in the calibration curve.

Once the calibration range has been established, a standard at the upper limit shall be prepared and analyzed using the normal calibration curve and must have a measured value within ± 10 % of the expected true value.

Note: This represents a deviation from EPA Method 6010C. Because a calibration range with a defined maximum concentration is used, there is no need to confirm the upper limit of the linear dynamic range.

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Additionally, the LOQ shall be verified by analyzing a blank spiked at 1 – 2 times the reporting limit and must have a recovery within ± 30 % of the expected value. If the LOQ cannot be verified, the reporting limit must be increased until the validity of the lower limit can be re-established.

7.1.4. Instrument Detection Limits (IDLs)

Instrument detection limits (IDLs) allow a user to evaluate the background noise inherent to a single instrument and are a function of the change in signal over time in the analyses of reagent blanks at the wavelength for each analyte. They are unrelated to reporting limits and should not be used to establish the reporting limit.

IDLs are determined by calculating the average of the standard deviations of three runs on non-consecutive days, with each run consisting of the analysis of seven consecutive measurements of a reagent blank solution. Each measurement must be performed as though it were a separate analytical sample; each blank must undergo any procedure normally performed between the analyses of samples.

The IDLs shall be determined as a part of the initial demonstration of proficiency and checked every six months by running a single set of seven blank samples and comparing the standard deviation to the established IDLs. If the check is not within the 95% confidence interval (see the SOP for EPA Method 6010C: ICP-AES Appendix B) for the established IDLs, the sample introduction system on the instrument shall be cleaned and a new set of IDLs established.

7.2. Instrument Operation

The following instrument QC shall be included with every analysis. The analysis data for all of the initial and subsequent calibration verification analyses listed below shall be kept on file with the sample analysis data. A summary of the required frequency of instrument verification analyses can be found in Table 3. A list of current concentrations used for instrument quality control can be found in Appendix B.

Note: Because the typical ICP-AES analytical method includes many elements, it is acceptable to ignore the failure of QC acceptance criteria for a specific analyte when that analyte is not of concern for the project goals for a given analysis (e.g. the analysis is specifically for phosphorus but antimony does not pass). However, effort shall be made to determine the cause of the QC failure and corrections shall be implemented prior to any future analyses.

7.2.1. Calibration Curve

To be considered acceptable, the calibration curve shall have a correlation coefficient greater than or equal to 0.998 for each target analyte. If the required linear response cannot be attained using three non-zero calibration standards, more standards shall be added, particularly at lower concentrations to better define the linear range and LOQ. The linear range may be narrowed to improve performance by removing the extreme upper and/or lower calibration points as

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long as three non-zero points remain and the non-linear upper and/or lower portions are removed.

7.2.2. Internal Standardization

The intensities of an internal standard must be monitored in every analysis. An internal standard is one or more elements that are both not found in the samples and verified to not cause an inter-element spectral interference to the samples, standards, and blanks. The addition of an internal standard to the samples ensures consistency in the analysis by correcting for small deviations in signal strength (see the SOP for EPA Method 6010C: ICP-AES Appendix B).

The concentration of internal standard shall fall within the normal calibration range of the instrument and must be added to all blanks, standards, and samples. This may be done by manual addition or using an on-line addition as part of the sample introduction system on the instrument. The online addition method is preferred because the constant pump rate adds exactly the same amount of internal standard to each sample analyses and does not risk the chance of "missing" a sample upon manual addition.

Internal standard recoveries shall fall within 70-130% of the intensity measured in the calibration blank. If the percent recovery of the internal standard in a sample falls below 70%, a significant matrix effect must be suspected. Under these conditions, the LOQ has degraded and the internal standard correction becomes questionable. If the percent recovery is above 130%, the presence of internal standard native to the sample must be suspected. These issues shall be addressed as follows.

- Make sure the poor recovery is not a result of an issue with the instrument (such as drift or sample introduction issues) by checking the internal standard intensities in the nearest standard or blank. If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, find and correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

- If there is no evidence of instrument-related issues, both matrix effects and native quantities of the internal sample need to be removed by dilution of the affected sample until the internal standard falls within the acceptable range (70-130%). Reported results must be corrected for all dilutions and a notation made about the matrix effect or native internal standard in the report.

7.2.3. Initial Calibration Verification

After initial calibration, the calibration curve shall be verified by the analysis of an initial calibration verification (ICV) standard, which shall be prepared from a second source (independent) material at or near the mid-range of the calibration curve. The acceptance criteria for the ICV standard is ± 10 % of its true value.

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If the recovery is outside of the acceptance criteria, the ICV standard shall be rerun once for confirmation and if recoveries are still not acceptable, the ICV standard shall be remade. If the calibration curve cannot be verified within the acceptable limits after remaking the ICV standard, the cause must be determined and the instrument must be recalibrated before analysis of samples may begin. Quantitative sample analyses shall not proceed for those analytes that fail to meet the acceptance criteria unless the results are flagged as estimated values.

7.2.4. Low-Level Calibration Verification

In addition to the ICV standard, an initial low-level calibration verification (LLCV) standard shall be prepared and analyzed prior to any samples. The LLCV standard shall also be analyzed every 10 samples and at the end of each analysis.

The LLCV standard shall be prepared at a concentration equal to the reporting limit from the same source as the calibration standards. If practicable, the LLCV standard should be the same solution as the lowest standard used during calibration. The acceptance criteria for the LLCV is ± 30 % of its true value. If the LLCV standard fails to meet the acceptance criteria, steps shall be taken to correct any problems up to and including recalibration as described in Section 7.2.8. All samples following the last acceptable LLCV must be reanalyzed.

7.2.5. Calibration Blank Verification

During the initial calibration verification, an initial calibration blank (ICB) must be analyzed. Also, after every ten samples and at the end of every analysis, a continuing calibration blank (CCB) must be analyzed. When practicable, this blank should be the same blank used as the initial calibration blank. The ICB/CCB must have a measured concentration less than one quarter (1/4) of the reporting limit for any desired analyte. If the ICB/CCB fails to meet the acceptance criteria, steps shall be taken to correct any problems up to and including recalibration as described in Section 7.2.8. All samples following the last acceptable ICB/CCB must be reanalyzed.

7.2.6. Continuing Calibration Verification

After every ten samples and at the end of every analysis, a continuing calibration verification (CCV) standard must be analyzed. The CCV standard shall be prepared from the same stock as the calibration standards at or near the mid-range of the calibration curve. If practicable, the CCV should be the same solution used as a mid-point used during calibration. The acceptance criteria for the CCV standard is ± 10 % of its true value. If the CCV fails to meet the acceptance criteria, steps shall be taken to correct any problems up to and including recalibration as described in Section 7.2.8. All samples following the last acceptable CCV must be reanalyzed.

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7.2.7. Interference Check/Inter-Element Correction (IEC) Verification

Whether or not inter-element corrections are applied to the sample, the absence of uncorrected interferences is necessary. This is monitored by the analysis of an interference check solution (also referred to as the IEC standard), which contains high concentrations of major components typical to most samples (>100 mg/L) to verify the absence of effects at the selected analytical wavelengths.

If analysis of the IEC standard results in a recovery outside of an acceptable range of ± 20 % of the true value, the analyte must be determined using an alternate analytical wavelength free of the interference or with the development. It is also acceptable to develop and apply an inter-element correction model for the specific interaction between analyte and interference (see the SOP for EPA Method 6010C: ICP-AES Section 4.2.2 and Appendix D).

This solution can also serve to check any inter-element corrections applied to the analysis, as long as all interfering elements in the IEC model are included as major components in the IEC standard. If the ± 20 % acceptance criteria cannot be achieved when the IEC model is applied, then the model either must be rebuilt (see the SOP for EPA Method 6010C: ICP-AES Appendix D) or the interference is deemed non-correctable and a different analytical wavelength must be chosen.

7.2.8. Instrument QC Failure

If any of the instrument QC samples fail to meet the criteria listed above, the sample shall be rerun. After 2 consecutive QC failures, an attempt to find and correct the cause of the failed QC must be made. The following represents a general order of corrections that do not require recalibration:

- Allow the system to rinse for 5 – 10 minutes and then reanalyze the QC sample.
- Re-prepare the QC sample from the same stock (or working standard) and analyze the new QC sample.
- Re-prepare the QC sample from an alternate stock (or fresh working standard) and analyze the new QC sample.

Reanalysis after a correction allows an additional 2 attempts before another correction must be attempted. If the QC sample still does not pass after the above corrections, a more significant issue is present which will likely require changes to the sample introduction system (and therefore recalibration). If recalibration is needed, the current analytical run must be aborted and all samples since last passing QC must be rerun after the issue causing the failed QC is found and resolved. Each correction made must be noted on the print-out of the raw data of the first re-analyzed QC sample for inclusion in the analytical file.

Note: The Winlab software includes an automated quality control system which is set up as part of instrument method parameters. When used, it automatically evaluates designated instrument quality control samples against user-set

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acceptance criteria and flags the QC sample as either "passed" or "failed" in the printed results summary. The "QC failed" notation does not invalidate the analysis of the samples. It only indicates that one or more elements did not meet the method-defined QC criteria and the data must be reviewed by the analyst before continuing with the analysis. If an active back-up spectral line passes the QC acceptance criteria (indicating interference on the primary line) or if the analyte with failed QC is not of concern, then the data can be used and analysis can continue. Otherwise, corrective steps shall be taken as described previously.

7.3. Method-Based Quality Control Samples

Quality control samples included in sample batches will vary based on project-specific requirements but will include some or all of the following. The quality control requirements of the project or specific sample preparation method shall supersede any requirements expressed in this section. A summary of the typical frequency of method-based quality control samples can be found in Table 3. A description of the calculations for percent recovery and relative percent difference (along with other relevant equations) can be found in the SOP for EPA Method 6010C: ICP-AES Appendix B.

Note: As described in Section 7.2, it is acceptable to ignore the failure of QC acceptance criteria for a specific analyte when that analyte is not of concern for the project goals for a given analysis.

7.3.1. Method Blank (MB)

Method blanks (MB) are necessary to monitor the sample preparation process for background contamination. At least one method blank must be prepared per batch of 20 samples using a mass of reagent water matching the mass of the samples which is then carried through the complete extraction, digestion, and/or other sample preparation process.

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 100 ppb for antimony, phosphorus, and iron and 250 ppb for aluminum, calcium, and magnesium. If the method blank cannot be considered acceptable, the method blank shall be re-run once, and if still unacceptable, then the entire sample batch must be reprepared and reanalyzed including all batch QC samples.

If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level then a notation of the sample data may be used despite the contamination of the method blank as long as it is accompanied by notation or flagging of the contamination in the report.

7.3.2. Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD)

A laboratory control sample (LCS) and a laboratory control sample duplicate (LCSD) must be prepared per batch of 20 samples by spiking reagent water with

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each analyte of interest at a concentration at or near the midpoint of the calibration range. The LCS/LCSD are then carried through the complete digestion and other sample preparation process along with the samples. The acceptance criteria for the LCS/LCSD is ± 20 % of the spiked value and the pair must have a relative percent difference (RPD) of ≤ 20 %. If the LCS or LCSD does not meet the acceptance criteria, it shall be re-run once, and if still unacceptable, the entire sample batch must be reprepared and reanalyzed including all batch QC samples.

The analyses of standard reference materials containing known amounts of analytes in the matrix of interest (if available) may be used as a substitute for the LCS; however, manufacturer-suggested acceptance criteria should be used in place of the standard acceptance criteria.

7.3.3. Duplicate (DUP) or Triplicate (TRI) Samples

The analysis of duplicate (DUP) or triplicate (TRI) samples is an essential measure of analytical precision in samples known to contain analytes of interest. Each sample batch should include at least two subsamples split from a single sample that undergo the same preparation and analysis steps. Samples may also be split into three for a more robust examination of analytical precision. The acceptance criteria for the sample duplicates is ≤ 20 % RPD. If three samples are analyzed, they must have a relative standard deviation (RSD) ≤ 20 % (see the SOP for EPA Method 6010C: ICP-AES Appendix B for formula).

Measured values for analytes that fall below the reporting limit should not be considered as criteria for acceptance or failure of the sample duplicates. If the sample duplicates or triplicates do not meet the acceptance criteria, the original sample must be examined to determine if the failure is due to issues with the digestion or an unavoidable lack of homogeneity in the sample. Failure to meet acceptance criteria due to an unavoidable lack of homogeneity must be noted in the final report. Otherwise the entire sample batch and all related QC samples must be reprepared and reanalyzed.

7.3.4. Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

It is important to document any potential changes in precision and bias due to matrix effects by the analysis of matrix spike (MS) and matrix spike duplicate (MSD) samples. In general, a sample batch should have at least one MS and one duplicate sample (if the samples are expected to contain the target analytes) or one MS and one MSD (if the samples are not expected to contain the target analytes). This may vary based on project and sample specific requirements, such as matrices where matrix spiking is ineffective due to the required dilution. In these cases, post digestion spiking is essential to monitor precision and bias (see Section 7.3.5).

MS/MSD samples are prepared by splitting a sample and spiking one (or more) portion(s) with a known concentration of each analyte of interest prior to sample preparation and analysis. If both MS/MSD samples are prepared, they must be spiked at the same concentration and with the same spiking material as the LCS

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for the sample batch. The spike concentration shall be at approximately mid-point of the calibration range. The acceptance criteria are ± 25 % of the spiked value for accuracy and of ≤ 20 % RPD for precision.

If the recovery and/or RPD are outside the laboratory control limits, post digestion spikes and serial dilutions shall be used to determine if the failure to meet acceptance criteria is due to matrix effects or other interferences. These tests shall be performed with each batch of samples that does not meet MS/MSD acceptance criteria. If matrix effects are confirmed, they must be documented in the final report along with the additional testing completed.

7.3.5. Post Digestion Spike (PS)

If MS/MSD recoveries are unacceptable, a post digestion spike (PS) sample shall be prepared and analyzed. The PS is prepared by spiking an additional portion of prepared sample (or its dilution) that was used to originally prepare the MS/MSD samples. If there is insufficient sample volume remaining from the original sample, another sample from the same preparation batch shall be used as an alternative. The spike concentration should fall between 10 and 100 times the reporting limit. The PS sample has acceptance criteria of ± 20 % of the spiked value. If this spike fails and the analyte concentrations are sufficiently high, a serial dilution shall be run on the sample to distinguish between matrix effects and interferences. If both the MS/MSD and the post digestion spike fail but the serial dilution passes, matrix effects are confirmed.

It is acceptable to prepare and analyze a PS sample at the same time as the original samples to minimize the need for recalibration and secondary analyses.

7.3.6. Serial Dilution (SD)

If the questionable analyte concentration is sufficiently high (at least a factor of 10 above the reporting limit after dilution), the analysis of a 1:5 serial dilution (SD) should agree within ± 10 % of the original value. If not, then potential interferences should be investigated. If the interference is the result of spectral overlap, the analyte concentration must either be determined at an alternate wavelength or an IEC model must be applied to the current wavelength and the sample must be reanalyzed.

It is acceptable to prepare and analyze a serial dilution sample at the same time as the original samples to minimize the need for recalibration and secondary analyses.

8. INSTRUMENT WARM-UP AND DAILY MAINTENANCE

For general information regarding instrument warm-up and daily maintenance, please refer to the SOP for EPA Method 6010C: ICP-AES Section 8.

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9. ANALYTICAL PROCEDURE

9.1. Sample Preparation

9.1.1. Fill out all the sample preparation information in the ICP-AES Analytical Run Log Sheet (See Figure 2).

9.1.2. Prepare the samples for analysis, including any necessary dilutions and post digestion spikes.

Note: The standard protocol for flame retardant samples is to take 4 mL of digestate and bring the volume up to 10 mL with DI water before analysis.

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.

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

9.2. Sample Information Entry

For general information regarding sample information entry, please refer to the SOP for EPA Method 6010C: ICP-AES Section 9.2.

9.3. Calibration

For general information regarding calibration, please refer to the SOP for EPA Method 6010C: ICP-AES Section 9.3.

9.4. Sample Analysis

For general information regarding sample analysis, please refer to the SOP for EPA Method 6010C: ICP-AES Section 9.4.

10. INSTRUMENT SHUTDOWN

For general information regarding instrument shutdown, please refer to the SOP for EPA Method 6010C: ICP-AES Section 10.

11. DATA ANALYSIS AND REPORTING

11.1. Data Analysis and QC Review

- All necessary 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.

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- Enter the sample mass and dilution information into the [Samples] tab.
- Check the [CV] and [QC] tabs to ensure all instrument and batch QC have met the appropriate criteria.
- 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. Please refer to the SOP for LIMS Report Generation for more details.

11.2. Reporting Data

A completed report packet shall include:

- The complete report form (including all relevant batch QC)
- A copy of the sample analysis request form (SAR)
- A copy of the authorization request form (ARF)
- A copy of all related sample receipt and chain-of-custody documentation, including any photographs taken upon receipt
- For each analytical run used in the report:
    - The hardcopy of the raw data for each analytical run used in the report (including the run sequence and any initialed notations regarding instrument QC failure)
    - A printed copy of the QC Analysis worksheet for each analytical run (including any initialed notations)
- A copy of the digestion log sheet for each digestion batch (if relevant)
- A copy of the ICP-AES Analytical Run Log Sheet (See Figure 2)
- All ICP-AES Standards Preparation Log Sheets (See Figure 1) associated with the analysis
- A copy of the certification for all standards used during digestion and analysis
- Any other notes collected during sample preparation or analysis

12. MAINTENANCE AND TROUBLESHOOTING

For general information regarding maintenance and troubleshooting, please refer to the SOP for EPA Method 6010C: ICP-AES Section 12 and Appendix D.

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13. REFERENCES

(1) Standard Operating Procedure for EPA Method 6010C: Inductively Coupled Plasma-Atomic Emission Spectroscopy, DCN: 03.6010.00, Revision No: 1 or current.

(2) Standard Operating Procedure for Acid Digestion of Flame Retardant Samples, DCN: 05.0033.00, Revision No: 0 or current.

(3) Current version of the Standard Operating Procedure for LIMS Report Generation.

(4) United States Environmental Protection Agency, “Method 6010C – Inductively Coupled Plasma-Atomic Emission Spectroscopy” from “Test Methods for the Evaluation of Waste”, SW-846. Revision 3. February 2007.

(5) Optima 7100, 7200, and 7300 Series Hardware Guide. PerkinElmer, Inc., June 2008.

(6) WinLab32 Software Guide. PerkinElmer, Inc. (accessed via WinLab32 program)

(7) S10 Auto-sampler for Atomic Spectroscopy: User’s Guide. PerkinElmer, Inc., December 2007.

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14. 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	0.0343	Antimony	206.8	Radial	0.0225

*Note: * IDLs were determined using data on February 3rd, 5th, and 10th 2015 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	Flow Rate	**Plasma**	
Plasma	15 L/min	RF Power	1300 watts
Auxiliary	0.2 L/min	View Distance	15 mm
Nebulizer	0.80 L/min	Aerosol Type	Wet
		Source Equilibration Delay	15 sec
Pump	Pump Rate	**Spectrometer**	
Flush	2.0 mL/min (for 20 sec)	Read Delay	60 sec
Sample	2.0 mL/min	Number of Reads	3
Rinse	1.5 mL/min (for 60 sec)	Background Correction	2-Point

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

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15. FIGURES

Figure 1: ICP-AES Standards Preparation Log Sheet

Lab Notebook # _____

ICP-AES Standards Preparation Log
Environmental Chemistry Lab, CA-DTSC

Page 1

Prep'd by:	Date Prep'd	Standard Name	Source			Preparation				Comments
			Stock Used	Lot #	Expires on:	According to SOP*?	Stock Vol (mL)	Final Vol (mL)	Final Conc.	

* If this box is checked, this standard was prepared according to the method described in the most current version of Appendix A of the SOP for ICP-AES analysis

Additional Comments and/or Calculations:

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Reviewed By/Date

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Figure 2: ICP-AES Analytical Run Log Sheet

Lab Notebook # _____

ICP-AES Analytical Run Log
Environmental Chemistry Lab, CA-DTSC

Page 1

Name of Analyst: _____ **Date of Analysis:** _____

Instrument: Optima 4300 ☐ **Digestion Method:** _____
Optima 7300 ☐ **Digestion Batch #:** _____

Sample Information File Name: _____
Results File Name: _____

Calibration included in results file? Yes ☐ No ☐
If no, name of results file that contains the calibration: _____

Spiking Solution: _____ Prepared: _____ Expires: _____

Sample	Digestate Volume (mL)	Spike Volume (mL)	Final Spike Concentration (ppm)	Final Volume (mL)	Dilution Factor

Comments:

Sample dilution and post digestion spike concentration calculations can be found in Appendix B of the ECL ICP-AES SOP.

Sample dilution and post digestion spike concentration calculations can be found in Appendix B of the ECL ICP-AES SOP.

Continued from page _____
Continued on page _____

_____
Analyst Signature / Date

DCN: 07.0012.00_Rev 0_12/31/2012

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16. 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 6010: ICP-AES in flame retardant samples.

How to Add the Universal Data Acquisition Function

- To add the Universal Data Acquisition function to an existing method, click the <**Method**> button at the top center in the main WinLab32 window. In the Open Method window, select a method file (the most recent method created to analyze flame retardant samples using this SOP) to edit the method and click <**OK**>.

- In the main WinLab32 window, click the <**MethEd**> 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>** and <**Method>** under the **File** menu.

- Please refer to the WinLab32 Software Guide for more details.

How to Process Data by Recalling Calibration

- In the main WinLab32 window, click the <**Method**> button at the top center. 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-AES) 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-AES) by clicking on <**Recall Calibration>** under the **Analysis** menu. In the Select Results Data Set window, select a data set and click <**OK**>.

- In the main WinLab32 window, click the <**Reproc**> icon to reprocess data.

- In the Data Reprocessing window, click the <**Browse**> button for "Data Set To Reprocess". In the Select Results Data Set window, select a flame retardant 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 <**Browse**> button for "Reprocessed Data Set". In the Select Results Data Set window, type "Name" and "Description" to be able

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to recognize the flame retardant data set after reprocessing by recalling a calibration and click <**OK**>.

- In the Data Reprocessing window, click the “Save Reprocessed Data” option.
- In the Data Reprocessing window, click the <**Reprocess**> button.
- In the main WinLab32 window, click the <**Results**> icon and print out the results.
- Please refer to the WinLab32 Software Guide for more details.

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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)	0.1 ppm P, Sb, and Fe; 0.25 ppm Al, Ca, and Mg
Inter-Element Correction Verification (IEC)	1 ppm P and Sb; 100 ppm Fe; 250 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 June 23, 2015.

Current Spiking Levels

Method-Based QC Samples	Concentrations
Laboratory Control Sample (LCS/LCSD) in digestate	12.5 ppm P and Sb
Laboratory Control Sample (LCS/LCSD) on ICP-AES	5 ppm P and Sb
Matrix Spike (MS/MSD) in digestate	12.5 ppm P and Sb
Matrix Spike (MS/MSD) on ICP-AES	5 ppm P and Sb
Post Digestion Spike (PS)	5 ppm P and Sb

Note: These concentrations are currently used for the method-based QC samples as of June 23, 2015.

Stock Solutions

Name	Analyte	Supplier	P/N
RICCA Phosphorus	10000 ppm P	RICCA Chemical Company	PP10KW
SPEX Phosphorus	1000 ppm P	SPEX CertiPrep	PLP9-2X
Ultra Antimony	10000 ppm Sb	Ultra Scientific	ICP-151
CPI Antimony	1000 ppm Sb	CPI International	4400-100023
RICCA Yttrium	1000 ppm Y	RICCA Chemical Company	PY1KN
CPI Majors	2000 ppm Fe; 5000 ppm Al, Ca, Mg	CPI International	4400-INTA1-500

Note: The stock solutions are currently in use and these concentration levels are current as of June 23, 2015.

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Solutions for Rinsing and Dilution

- **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 in Room 174.

- **Concentrated Nitric Acid (HNO_3)**

  - EMD, Omni Trace, NX0407/2
  - BDH, Aristar Plus, 87003-261

- **2% (v/v) HNO_3 in Reagent Water as Instrument Rinse Solution**

  Dilute 40 mL of concentrated HNO_3 to a final volume of 2 L with reagent water in a 2-L volumetric flask and mix thoroughly.

- **5% (v/v) HNO_3 in Reagent Water for Mixing Standards**

  Dilute 100 mL of concentrated HNO_3 to a final volume of 2 L with reagent water in a 2-L volumetric flask and mix thoroughly. All subsequent uses of the term "5% HNO3" refer to this solution.

Calibration Standards

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

  The calibration blank shall be an aliquot of the same 5% HNO_3 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 three times with 5 % HNO_3 solution. Pipette 5 mL each of the RICCA phosphorus stock and Ultra antimony stock into the volumetric flask. Bring to volume with 5 % HNO_3 solution and mix thoroughly. Fill out the ICP-AES Standards Preparation Log Book (See Figure 1). This P & Sb Spike 500 contains 500 ppm of P and Sb and will expire 30 days from the preparation date.

  Note: The expiration date can be extended beyond 30 days 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.

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- **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 CPI Majors stock into a 100-mL volumetric flask. Bring to volume using 5% HNO_3 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 30 days from the preparation date.

- **Instrument Calibration Standards**

  A series of calibration standards at 0.1, 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)
0.1	0.100 mL of P & Sb Cal 100	100
0.5	0.500 mL of P & Sb Cal 100	100
1.0	1.00 mL of P & Sb Cal 100	100
5.0	5.00 mL of P & Sb Cal 100	100
20	10.0 mL of P & Sb Cal 100	100
50	10.0 mL of P & Sb Spike 500; 2.50 mL of CPI Majors	100
100	20.0 mL of P & Sb Spike 500; 5.00 mL of CPI Majors	100

  Bring the standards to volume using 5% HNO_3 solution. Standards may be made to final concentrations and/or volumes other than those shown above as needed. These standards will expire 30 days from the preparation date, but are generally prepared fresh as needed for analysis.

Calibration Verification Solutions

- **50 ppm Yttrium Internal Standard**

  Dilute 50 mL of the 1000 ppm Y Stock to a final volume of 1 L using 5% HNO_3 solution in a volumetric flask. Mix thoroughly and transfer into 1 L plastic storage bottle.

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

  Dilute 0.5 mL of the 1000 ppm SPEX P stock and the 1000 ppm CPI Sb stock to a final volume of 100 mL using 5% HNO_3 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 30 days from the preparation date.

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

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

Note: Currently, 0.1 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 5 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% HNO_3 and mix thoroughly. This P & Sb IEC standard contains 1.0 ppm of P and Sb, 100 ppm of Fe, and 250 ppm of Al, Ca, and Mg and will expire 30 days from the preparation date.

Auto-sampler Placement

- **Auto-sampler Placement of Calibration and Verification Standards**

  The calibration blank, the calibration standards, the ICV solution, and the IEC solution shall be placed in the auto-sampler rack in the following locations:

A/S Loc	Standard	A/S Loc	Standard
1	ICB/CCB	6	20 ppm Std
2	0.1 ppm Std/LLCV	7	50 ppm Std
3	0.5 ppm Std	8	100 ppm Std
4	1.0 ppm Std	9	ICV
5	5.0 ppm Std/CCV	10	IEC

Note: The ICV and IEC solutions are held in a 15-mL sample tube rather than the normal 50-mL standards tube.

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17. REVISION HISTORY

Revision History:

Revision	Date	Responsible Person	Description of Change
0	June 2015	Sayaka Takaku-Pugh	New SOP developed to determine phosphorus in flame retardant samples by ICP-AES

18. ANNUAL REVIEW

Signatures	Date