(4) Use a hydrophobic sorbent in a sealed sorbent module. Note that this sorbent module is intended to be the final stage for collecting the SVOC sample and should be sized accordingly. We recommend sizing the module to hold 40 g of XAD–2 along with PUF plugs at either end of the module, noting that you may vary the mass of XAD used for testing based on the anticipated SVOC emission concentration and sample flow rate.

(5) Include a condensate trap to separate the aqueous liquid phase from the gas stream. We recommend using a peristaltic pump to remove water from the condensate trap over the course of the test to prevent build-up of the condensate. Note that for some tests it may be appropriate to collect this water for analysis.

(d) *Sampler flow control.* For testing using the recommended filter and sorbent module sizes, we recommend targeting an average sample flow rate of 70 liters per minute to maximize SVOC collection. The sampler must be designed to maintain proportional sampling throughout the test. Verify proportional sampling after an emission test as described in §1065.545.

(e) *Water bath.* Design the sample system with a water bath in which the cooling coil, sorbent module, and condensate trap will be submerged. Use a heat exchanger or ice to maintain the bath temperature at (3 to 7) °C.

[79 FR 23820, Apr. 28, 2014, as amended at 81 FR 74195, Oct. 25, 2016]

§1065.1107 Sample media and sample system preparation; sample system assembly.

This section describes the appropriate types of sample media and the cleaning procedure required to prepare the media and wetted sample surfaces for sampling.

(a) *Sample media.* The sampling system uses two types of sample media in series: The first to simultaneously capture the PM and associated particle phase SVOCs, and a second to capture SVOCs that remain in the gas phase, as follows:

(1) For capturing PM, we recommend using pure quartz filters with no binder if you are not analyzing separately for SVOCs in gas and particle phases. If you are analyzing separately, you must use polytetrafluoroethylene (PTFE) filters with PTFE support. Select the filter diameter to minimize filter change intervals, accounting for the expected PM emission rate, sample flow rate. Note that when repeating test cycles to increase sample mass, you may replace the filter without replacing the sorbent or otherwise disassembling the batch sampler. In those cases, include all filters in the extraction.

(2) For capturing gaseous SVOCs, utilize XAD–2 resin with or without PUF plugs. Note that two PUF plugs are typically used to contain the XAD–2 resin in the sorbent module.

(b) *Sample media and sampler preparation.* Prepare pre-cleaned PM filters and pre-cleaned PUF plugs/XAD–2 as needed. Store sample media in containers protected from light and ambient air if you do not use them immediately after cleaning. Use the following preparation procedure, or an analogous procedure with different solvents and extraction times:

(1) Pre-clean the filters via Soxhlet extraction with methylene chloride for 24 hours and dry over dry nitrogen in a low-temperature vacuum oven.

(2) Pre-clean PUF and XAD–2 with a series of Soxhlet extractions: 8 hours with water, 22 hours with methanol, 22 hours with methylene chloride, and 22 hours with toluene, followed by drying with nitrogen.

(3) Clean sampler components, including the probe, filter holder, condenser, sorbent module, and condensate collection vessel by rinsing three times with methylene chloride and then three times with toluene. Prepare pre-cleaned aluminum foil for capping the probe inlet of the sampler after the sampling system has been assembled.

(c) *Sorbent spiking.* Use good engineering judgment to verify the extent to which your extraction methods recover SVOCs absorbed on the sample media. We recommend spiking the XAD–2 resin with a surrogate standard before testing with a carbon-13 or hydrogen-2 isotopically labeled standard for each of the class of analytes targeted for analysis. Perform this spiking as follows:

(1) Insert the lower PUF plug into the bottom of the sorbent module.

(2) Add half of one portion of XAD–2 resin to the module and spike the XAD–2 in the module with the standard.

(3) Wait 1 hour for the solvent from the standard(s) to evaporate, add the remaining 20 g of the XAD–2 resin to the module, and then insert a PUF plug in the top of the sorbent module.

(4) Cover the inlet and outlet of the sorbent module with pre-cleaned aluminum foil.

(d) *Sampling system assembly*. After preparing the sample media and the sampler, assemble the condensate trap, cooling coil, filter holder with filter, sample probe, and sorbent module, then lower the assembly into the reservoir. Cover the probe inlet with pre-cleaned aluminum foil.

[79 FR 23820, Apr. 28, 2014, as amended at 81 FR 74195, Oct. 25, 2016]

§ 1065.1109 Post-test sampler disassembly and sample extraction.

This section describes the process for disassembling and rinsing the sampling system and extracting and cleaning up the sample.

(a) *Sampling system disassembly*. Disassemble the sampling system in a clean environment as follows after the test:

(1) Remove the PM filter, PUF plugs, and all the XAD–2 from the sampling system and store them at or below 5 °C until analysis.

(2) Rinse sampling system wetted surfaces upstream of the condensate trap with acetone followed by toluene (or a comparable solvent system), ensuring that all the solvent remaining in liquid phase is collected (note that a fraction of the acetone and toluene will likely be lost to evaporation during mixing). Rinse with solvent volumes that are sufficient to cover all the surfaces exposed to the sample during testing. We recommend three fresh solvent rinses with acetone and two with toluene. We recommend rinse volumes of 60 ml per rinse for all sampling system components except the condenser coil, of which you should use 200 ml per rinse. Keep the acetone rinsate separate from the toluene rinsate to the extent practicable. Rinsate fractions should be stored separately in glass bottles that have been pre-rinsed with acetone, hexane, and toluene (or purchase pre-cleaned bottles).

(3) Use good engineering judgment to determine if you should analyze the aqueous condensate phase for SVOCs. If you determine that analysis is necessary, use toluene to perform a liquid-liquid extraction of the SVOCs from the collected aqueous condensate using a separatory funnel or an equivalent method. Add the toluene from this aqueous extraction to the toluene rinsate fraction described in paragraph (a)(2) of this section.

(4) Reduce rinsate solvent volumes as needed using a Kuderna-Danish concentrator or rotary evaporator and retain these rinse solvents for reuse during sample media extraction for the same test. Be careful to avoid loss of low molecular weight analytes when concentrating with rotary evaporation.

(b) *Sample extraction*. Extract the SVOCs from the sorbent using Soxhlet extraction as described in this paragraph (b). Two 16 hour extractions are necessary to accommodate the Soxhlet extractions of all SVOCs from a single sample. This reduces the possibility of losing low molecular weight SVOCs and promotes water removal. We recommend performing the first extraction with acetone/hexane and the second using toluene (or an equivalent solvent system). You may alternatively use an equivalent method such as an automated solvent extractor.

(1) We recommend equipping the Soxhlet extractor with a Dean-Stark trap to facilitate removal of residual water from the sampling system rinse. The Soxhlet apparatus must be large enough to allow extraction of the PUF, XAD–2, and filter in a single batch. Include in the extractor setup a glass thimble with a coarse or extra coarse sintered glass bottom. Pre-clean the extractor using proper glass-cleaning procedures. We recommend that the Soxhlet apparatus be cleaned with a (4 to 8) hour Soxhlet extraction with methylene chloride at a cycling rate of three cycles per hour. Discard the solvent used for pre-cleaning (no analysis is necessary).

(2) Load the extractor thimble before placing it in the extractor by first rolling the PM filter around the inner circumference of the thimble, with the

sampled side facing in. Push one PUF plug down into the bottom of the thimble, add approximately half of the XAD–2, and then spike the XAD–2 in the thimble with the isotopically labeled extraction standards of known mass. Target the center of the XAD–2 bed for delivering the extraction standard. We recommend using multiple isotopically labeled extraction standards that cover the range of target analytes. This generally means that you should use isotopically labeled standards at least for the lowest and highest molecular weight analytes for each category of compounds (such as PAHs and dioxins). These extraction standards monitor the efficiency of the extraction and are also used to determine analyte concentrations after analysis. Upon completion of spiking, add the remaining XAD–2 to the thimble, insert the remaining PUF plug, and place the thimble into the extractor. Note that if you are collecting and analyzing for SVOCs in gas and particle phases, perform separate extractions for the filter and XAD–2.

(3) For the initial extraction, combine the concentrated acetone rinses (from the sampling system in paragraph (a) of this section) with enough hexane to bring the solvent volume up to the target level of 700 ml. Assemble the extractor and turn on the heating controls and cooling water. Allow the sample to reflux for 16 hours with the rheostat adjusted to cycle the extraction at a rate of (3.0 ±0.5) cycles per hour. Drain the water from the Dean-Stark trap as it accumulates by opening the stopcock on the trap. Set aside the water for analysis or discard it. In most cases, any water present will be removed within approximately 2 hours after starting the extraction.

(4) After completing the initial extraction, remove the solvent and concentrate it to (4.0 ±0.5) ml using a Kuderna-Danish concentrator that includes a condenser such as a three-ball Snyder column with venting dimples and a graduated collection tube. Hold the water bath temperature at (75 to 80) °C. Using this concentrator will minimize evaporative loss of analytes with lower molecular weight.

(i) Rinse the round bottom flask of the extractor with (60 to 100) ml of hexane and add the rinsate to this concentrated extract.

(ii) Concentrate the mixture to (4 ±0.5) ml using a Kuderna-Danish concentrator or similar apparatus.

(iii) Repeat the steps in paragraphs (b)(4)(i) and (ii) of this section three times, or as necessary to remove all the residual solvent from the round bottom flask of the extractor, concentrating the final rinsate to (4 ±0.5) ml.

(5) For the second extraction, combine the toluene rinses (from the sampling system in paragraph (a) of this section) with any additional toluene needed to bring the solvent volume up to the target level of 700 ml. As noted in paragraph (a) of this section, you may need to concentrate the rinsate before adding it to the extraction apparatus if the rinsate solvent volume is too large. Allow the sample to reflux for 16 hours with the rheostat adjusted to cycle the extraction at a rate of (3.0 ±0.5) cycles per hour. Check the Dean-Stark trap for water during the first 2 hours of the extraction (though little or no water should be present during this stage).

(6) Upon completion of the second extraction, remove the solvent and concentrate it to (4 ±0.5) ml as described in paragraph (b)(4) of this section. Using hexane from paragraph (b)(4) of this section as the rinse solvent effectively performs a solvent exchange of toluene with hexane.

(7) Combine the concentrated extract from paragraph (b)(4) of this section with the concentrated extract from paragraph (b)(6) of this section. Divide the extract into a number of fractions based on the number of analyses you need to perform. Perform the separate sample clean-up described in paragraph (c) of this section as needed for each fraction.

(c) *Sample clean-up.* This paragraph (c) describes how to perform sample cleaning to remove from the sample extract any solids and any SVOCs that will not be analyzed. This process, known as ''sample clean-up'', reduces the potential for interference or co-elution of peaks during analytical analysis. Before performing the sample clean-up, spike the extract with an alternate standard that contains a known mass of isotopically labeled

compounds that are identical to the target analytes (except for the labeling). The category of the target analyte compounds (such as PAHs or dioxin) will determine the number of compounds that make up the standard. For example, PAHs require the use of four compounds in the alternate standard to cover the four basic ring structures of PAHs (2-ring, 3-ring, 4-ring, and 5-ring structures). These alternate standards are used to monitor the efficiency of the clean-up procedure. Before sample clean-up, concentrate the fractionated sample to about 2 ml with a Kuderna-Danish concentrator or rotary evaporator, and then transfer the extract to an 8 ml test tube with hexane rinse. Concentrate it to a volume of about 1 ml using a Kuderna-Danish concentrator. Use good engineering judgment to select an appropriate column chromatographic clean-up option for your target analytes. Note that these clean-up techniques generally remove compounds based on their polarity. The following procedures are examples of clean-up techniques for PAHs and nPAHs.

(1) *PAH clean-up.* The following method is appropriate for clean-up of extracts intended for analysis of PAHs:

(i) Pack a glass gravity column (250 mm × 10 mm recommended) by inserting a clean glass wool plug into the bottom of the column and add 10 g of activated silica gel in methylene chloride. Tap the column to settle the silica gel and then add a 1 cm layer of anhydrous sodium sulfate. Verify the volume of solvent required to completely elute all the PAHs and adjust the weight of the silica gel accordingly to account for variations among batches of silica gel that may affect the elution volume of the various PAHs.

(ii) Elute the column with 40 ml of hexane. The rate for all elutions should be about 2 ml/min. You may increase the elution rate by using dry air or nitrogen to maintain the headspace slightly above atmospheric pressure. Discard the eluate just before exposing the sodium sulfate layer to the air or nitrogen and transfer the 1 ml sample extract onto the column using two additional 2 ml rinses of hexane. Just before exposing the sodium sulfate layer to the air or nitrogen, begin elution of the column with 25 ml of hexane followed by 25 ml of 40 volume % methylene chloride in hexane. Collect the entire eluate and concentrate it to about 5 ml using the Kuderna-Danish concentrator or a rotary evaporator. Make sure not to evaporate all the solvent from the extract during the concentration process. Transfer the eluate to a small sample vial using a hexane rinse and concentrate it to 100 µl using a stream of nitrogen without violently disturbing the solvent. Store the extracts in a refrigerator at or below 4 °C, and away from light.

(2) *nPAH clean up.* The following procedure, adapted from ''Determination and Comparison of Nitrated-Polycyclic Aromatic Hydrocarbons Measured in Air and Diesel Particulate Reference Materials'' (Bamford, H.A., *et al*, Chemosphere, Vol. 50, Issue 5, pages 575–587), is an appropriate method to clean up extracts intended for analysis of nPAHs:

(i) Condition an aminopropyl solid phase extraction (SPE) cartridge by eluting it with 20 ml of 20 volume % methylene chloride in hexane. Transfer the extract quantitatively to the SPE cartridge with at least two methylene chloride rinses. Elute the extract through the SPE cartridge by using 40 ml of 20 volume % methylene chloride in hexane to minimize potential interference of polar constituents, and then reduce the extract to 0.5 ml in hexane and subject it to normal-phase liquid chromatography using a pre-prepared 9.6 mm × 25 cm semi-preparative Chromegabond® amino/cyano column (5 µm particle size) to isolate the nPAH fraction. The mobile phase is 20 volume % methylene chloride in hexane at a constant flow rate of 5 ml per minute. Back-flash the column with 60 ml of methylene chloride and then condition it with 200 ml of 20 volume % methylene chloride in hexane before each injection. Collect the effluent and concentrate it to about 2 ml using the Kuderna-Danish concentrator or a rotary evaporator. Transfer it to a minivial using a hexane rinse and concentrate it to 100 µl using a gentle stream of nitrogen. Store the extracts at or below 4 °C, and away from light.

(ii) [Reserved]

[79 FR 23820, Apr. 28, 2014, as amended at 81 FR 74195, Oct. 25, 2016]

§ 1065.1111 Sample analysis.

This subpart does not specify chromatographic or analytical methods to analyze extracts, because the appropriateness of such methods is highly dependent on the nature of the target analytes. However, we recommend that you spike the extract with an injection standard that contains a known mass of an isotopically labeled compound that is identical to one of the target analytes (except for labeling). This injection standard allows you to monitor the efficiency of the analytical process by verifying the volume of sample injected for analysis.

VANADIUM SUBLIMATION IN SCR CATALYSTS

SOURCE: Sections 1065.1113 through 1065.1119 appear at 88 FR 4691, Jan. 24, 2023, unless otherwise noted.

§ 1065.1113 General provisions related to vanadium sublimation temperatures in SCR catalysts.

Sections 1065.1113 through 1065.1121 specify procedures for determining vanadium emissions from a catalyst based on catalyst temperature. Vanadium can be emitted from the surface of SCR catalysts at temperatures above 550 °C, dependent on the catalyst formulation. These procedures are appropriate for measuring the vanadium sublimation product from a reactor by sampling onto an equivalent mass of alumina and performing analysis by Inductively Coupled Plasma—Optical Emission Spectroscopy (ICP–OES). Follow standard analytic chemistry methods for any aspects of the analysis that are not specified.

(a) The procedure is adapted from ''Behavior of Titania-supported Vanadia and Tungsta SCR Catalysts at High Temperatures in Reactant Streams: Tungsten and Vanadium Oxide and Hydroxide Vapor Pressure Reduction by Surficial Stabilization'' (Chapman, D.M., Applied Catalysis A: General, 2011, 392, 143–150) with modifications to the acid digestion method from ''Measuring the trace elemental composition of size-resolved airborne particles'' (Herner, J.D. *et al*, Environmental Science and Technology, 2006, 40, 1925–1933).

(b) Laboratory cleanliness is especially important throughout vanadium testing. Thoroughly clean all sampling system components and glassware before testing to avoid sample contamination.

§ 1065.1115 Reactor design and setup.

Vanadium measurements rely on a reactor that adsorbs sublimation vapors of vanadium onto an alumina capture bed with high surface area.

(a) Configure the reactor with the alumina capture bed downstream of the catalyst in the reactor's hot zone to adsorb vanadium vapors at high temperature. You may use quartz beads upstream of the catalyst to help stabilize reactor gas temperatures. Select an alumina material and design the reactor to minimize sintering of the alumina. For a 1-inch diameter reactor, use 4 to 5 g of ⅛ inch extrudates or -14/+24 mesh (approximately 0.7 to 1.4 mm) gamma alumina (such as Alfa Aesar, aluminum oxide, gamma, catalyst support, high surface area, bimodal). Position the alumina downstream from either an equivalent amount of -14/+24 mesh catalyst sample or an approximately 1-inch diameter by 1 to 3-inch long catalyst-coated monolith sample cored from the production-intent vanadium catalyst substrate. Separate the alumina from the catalyst with a 0.2 to 0.4 g plug of quartz wool. Place a short 4 g plug of quartz wool downstream of the alumina to maintain the position of that bed. Use good engineering judgment to adjust as appropriate for reactors of different sizes.

(b) Include the quartz wool with the capture bed to measure vanadium content. We recommend analyzing the downstream quartz wool separately from the alumina to see if the alumina fails to capture some residual vanadium.

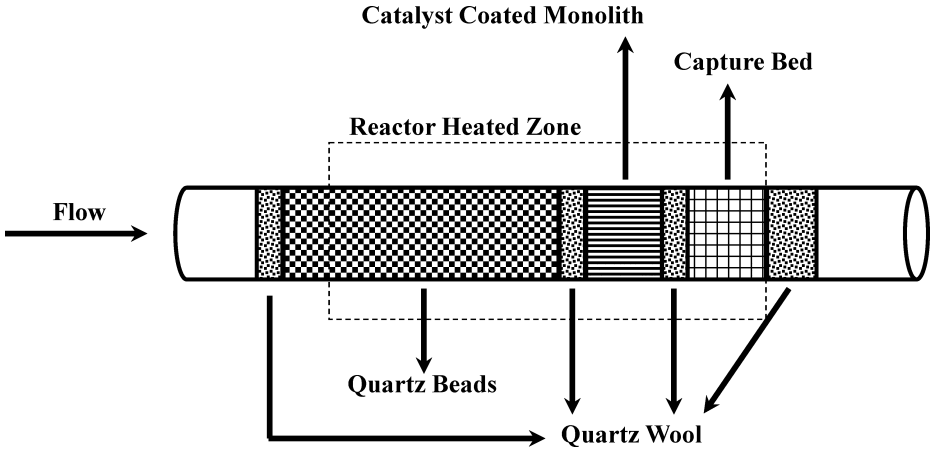
(c) Configure the reactor such that both the sample and capture beds are in the reactor's hot zone. Design the reactor to maintain similar temperatures in the capture bed and catalyst. Monitor the catalyst and alumina temperatures with Type K thermocouples

inserted into a thermocouple well that is in contact with the catalyst sample bed.

(d) If there is a risk that the quartz wool and capture bed are not able to collect all the vanadium, configure the reactor with an additional capture bed and quartz wool plug just outside the hot zone and analyze the additional capture bed and quartz wool separately.

(e) An example of a catalyst-coated monolith and capture bed arrangement in the reactor tube are shown in the following figure:

FIGURE 1 TO PARAGRAPH (E) OF §1065.1115— EXAMPLE OF REACTOR SETUP



(f) You may need to account for vanadium-loaded particles contaminating catalyst-coated monoliths as a result of physical abrasion. To do this, determine how much titanium is in the capture bed and compare to an alumina blank. Using these values and available information about the ratio of vanadium to titanium in the catalyst, subtract the mass of vanadium catalyst material associated with the catalyst particles from the total measured vanadium on the capture bed to determine the vanadium recovered due to sublimation.

§1065.1117 Reactor aging cycle for determination of vanadium sublimation temperature.

This section describes the conditions and process required to operate the reactor described in §1065.1115 for collection of the vanadium sublimation samples for determination of vanadium sublimation temperature. The reactor aging cycle constitutes the process of testing the catalyst sample over all the test conditions described in paragraph (b) of this section.

(a) Set up the reactor to flow gases with a space velocity of at least 35,000/hr with a pressure drop across the catalyst and capture beds less than 35 kPa. Use test gases meeting the following specifications, noting that not all gases will be used at the same time:

(1) 5 vol% O_2, balance N_2.

(2) NO, balance N_2. Use an NO concentration of (200 to 500) ppm.

(3) NH_3, balance N_2. Use an NH_3 concentration of (200 to 500) ppm.

(b) Perform testing as follows:

(1) Add a new catalyst sample and capture bed into the reactor as described in §1065.1113. Heat the reactor to 550 °C while flowing the oxygen blend specified in paragraph (a)(1) of this section as a pretest gas mixture.