EXTRACTION OF SEMIVOLATILE ANALYTES COLLECTED USING METHOD 0010 (MODIFIED METHOD 5 SAMPLING TRAIN)

1.0 SCOPE AND APPLICATION

1.1 This method describes the extraction of semivolatile organic compounds from samples collected by Method 0010. This method replaces Section 8.1 of Method 0010 (Modified Method 5 Sampling Train, also known as SemiVOST). Section 8.1 of Method 0010 addresses preparation of Method 0010 train components for analysis with very little detail.

1.2 Although this sample preparation technique is intended primarily for gas chromatography/mass spectrometric (GC/MS) analysis following Method 8270, the extracts prepared according to this method may be used with other analytical methods. The Method 0010 sampling train collects semivolatile organic compounds with boiling points above 100°C. Some of these semivolatile organic compounds may not be amenable to gas chromatography and will require the application of high performance liquid chromatography (HPLC) for quantitative analysis. The use of HPLC coupled with mass spectrometry (HPLC/MS) is an analytical technique that may also be applied. A solvent exchange from methylene chloride to a more polar solvent such as acetonitrile or extraction with a solvent other than methylene chloride will probably be required for successful application of HPLC techniques. Some semivolatile analytes may require derivatization for successful GC/MS analysis.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the extraction and concentration of semivolatile organic compounds from the components of Method 0010 trains. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Samples generated by the Method 0010 Sampling Train (Method 0010 Sampling Train, Figure 1) are separated into six parts:

a) a particulate matter filter (labeled in Method 0010 as Container No. 1);

b) a front half rinse (labeled in Method 0010 as Container No. 2);

c) condenser rinse and rinse of all sampling train components located between the filter and the sorbent module (labeled in Method 0010 as Container No. 5);

d) sorbent trap section of the organic module (labeled in Method 0010 as Container No. 3);

e) any condensate and condensate rinse (labeled in Method 0010 as Container No. 4); and

f) silica gel (labeled in Method 0010 as Container No. 6).

2.2 The overall sample preparation scheme (flowchart) is shown in Figure 3. The six parts recovered from the Method 0010 sampling train yield three 5-mL extracts to be analyzed according to the analytical procedures of Method 8270.

2.2.1 The particulate matter filter is extracted by Soxhlet (Method 3540, with exceptions as noted).

2.2.2 The front half rinse is filtered, and any filtrate is added to the particulate matter filter for Soxhlet extraction. The front half rinse is a 50:50 mixture of methanol and methylene chloride generated by rinsing the probe and the front half of the filter holder in the Method 0010 train. The front half rinse is extracted with methylene chloride by separatory funnel (Method 3510, with exceptions as noted) after sufficient organic-free reagent water has been added to make the methylene chloride separate as a distinct phase from the methanol/water.

2.2.3 The extracts from the filter and front half rinse are combined, moisture is removed by filtering through anhydrous sodium sulfate (Na_2SO_4), and the combined extract is concentrated using a Kuderna-Danish (K-D) sample concentrator (Method 3540) to a final volume of 5 mL. The final sample concentration to 5 mL can be performed more accurately by reducing the volume of the sample using a gentle stream of nitrogen or by using a micro-K-D.

2.2.4 The condensate and condensate rinse fractions consist of the aqueous contents of the first impinger of the Method 0010 sampling train and the 50:50 methanol/methylene chloride rinse of the first impinger of the Method 0010 sampling train. The condensate and condensate rinse fractions are combined and extracted with methylene chloride using a separatory funnel after sufficient organic-free reagent water has been added to make the methylene chloride separate from the methanol/water following the procedures of Method 3510 (with exceptions as noted).

2.2.5 After an initial methylene chloride extraction without pH adjustment, the pH of the combined condensate/condensate rinse fraction is determined. If the condensate/condensate rinse fraction is acid (pH < 7), the pH is adjusted to a level less than 2 and the methylene chloride extraction is repeated. The pH of the condensate/condensate rinse fraction is then made basic (pH > 12), and the methylene chloride extraction is repeated. The methylene chloride extracts are combined, and moisture is removed by filtration through a bed of anhydrous Na_2SO_4. If the condensate/condensate rinse fraction is found to be basic after the initial methylene chloride extraction, the pH adjustment sequence is reversed: a basic extraction is performed prior to an acid extraction, the methylene chloride extracts are combined, the moisture is removed, and the extract is concentrated to a volume of 5 mL.

2.2.6 The XAD-2® sampling module is combined with the filter holder back half rinse and the 50:50 methylene chloride/methanol condenser rinse and extracted by Soxhlet (Method 3540, with exceptions as noted). Organic-free reagent water is added to the extract to ensure the separation of methanol/water from the methylene chloride, and a water extraction of the methylene chloride extract is performed. Moisture is removed from the methylene chloride extract, which is then concentrated to a final volume of 5 mL for analysis.

2.2.7 The contents of the remaining impingers are usually archived, but may be extracted by separatory funnel. The silica gel is reused after regeneration by heating to remove moisture.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by preparing and analyzing laboratory method (or reagent) blanks.

3.1.1 Glassware must be cleaned thoroughly before using. The glassware should be washed with laboratory detergent in hot water followed by rinsing with tap water and distilled water. The glassware may be cleaned by baking in a glassware oven at 400°C for at least one hour. After the glassware has cooled, the glassware should be rinsed three times with methanol and three times with methylene chloride. Volumetric glassware should not be heated to 400°C. Rather, after washing and rinsing, volumetric glassware may be rinsed with methanol followed by methylene chloride and allowed to dry in air.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems in sample analysis.

3.2 Matrix interferences in the analysis may be caused by components of the sampling matrix that are extracted from the samples. If matrix interferences interfere with the analysis, sample cleanup procedures (e.g., Method 3620 or Method 3610) may be employed to remove or mitigate the interferences.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 50 mm I.D., with 500-mL round bottom flask and condenser. Larger equipment is acceptable if appropriate to the amount of sorbent.

4.2 Boiling chips - Polytetrafluoroethylene (PTFE), solvent rinsed with methylene chloride, approximately 10/40 mesh.

4.3 Forceps - Rinsed with methylene chloride before use.

4.4 Separatory funnel - 250-mL or larger, with PTFE stopcock.

4.5 Amber glass jar - 500-mL with PTFE-lined screw cap.

4.6 Glass funnel - Long stem.

4.7 Kuderna-Danish (K-D) apparatus.

4.7.1 Concentrator tube - 10-mL graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.7.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.7.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.7.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

NOTE: The glassware in Sec. 4.7 is recommended for the purpose of solvent recovery during the concentration procedures (Sec. 7.2.3 and 7.3.4) requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.8 Solvent vapor recovery system - (Kontes 545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.9 Glass wool - Non-silanized, pre-cleaned by Soxhlet extraction with methylene chloride. Air dry, store in pre-cleaned 500-mL jar.

4.10 Vials - 7- to 10-mL capacity, calibrated (calibrated centrifuge tubes may also be used).

4.11 Heating mantle - Rheostat-controlled.

4.12 Water bath - Heated, with concentric ring cover, capable of temperature control 80°C ± 5°C. The water bath should be used in a hood.

4.13 Gas-tight syringe - 5-mL to 10-mL capacity. Gas-tight syringes have a glass barrel, with a PTFE plunger to form an effective seal. The lack of contact with metal and the sealing properties make these syringes very useful for transferring liquid solutions.

4.14 Nitrogen blowdown apparatus - Analytical evaporator such as The Meyer N-EVAP Model 111 (Organomation Associates Inc., South Berlin, MA 01549) or equivalent.

4.15 Filter - Glass- or quartz-fiber filters, without organic binder. The filters should be the same as those used in the Method 0010 sampling train.

4.16 Wide range pH paper.

4.17 Rubber pipet filler bulb - for optional sorbent transfer procedure.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without compromising the integrity of the sample.

5.2 Methanol, CH_3OH - Pesticide quality or equivalent.

5.3 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.4 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.5 Sodium hydroxide solution (10 Molar) - Dissolve 40 g of sodium hydroxide (NaOH, ACS reagent grade) in organic-free reagent water and dilute to 100 mL.

5.6 Sulfuric acid (9 Molar), H_2SO_4 - Slowly add 50 mL of concentrated 18 M H_2SO_4 (ACS reagent grade, specific gravity 1.84) to 50 mL of organic-free reagent water.

5.7 Sodium sulfate, Na_2SO_4 - ACS, reagent grade, granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray.

5.8 Surrogate stock solution - Either surrogates (e.g., the surrogates used in Method 8270) or isotopically-labeled analogs of the compounds of interest should be spiked into the Method 0010 train components prior to extraction. Both surrogate and isotopically-labeled analogs may be used, if desired. A surrogate (i.e., a compound not expected to occur in an environmental sample but chemically similar to analytes) should be added to each sample, blank, and method spike just prior to extraction. The recovery of the surrogate is used to monitor for unusual matrix effects or sample processing errors. Normally three or more surrogates are added for each analyte group. The surrogate stock solution may be prepared from pure standard materials or purchased as a certified solution. Prepare the stock solution in methylene chloride, using assayed liquids or solids, as appropriate.

5.8.1 The following compounds are the surrogates recommended in Method 8270:

Acid	Base/Neutral
2-Fluorophenol	2-Fluorobiphenyl
2,4,6-Tribromophenol	Nitrobenzene-d_5
Phenol-d_6	Terphenyl-d_{14}

5.8.2 Prepare a surrogate stock solution in methylene chloride that contains the surrogate compounds at a concentration of 5000 µg/mL for the acidic compounds, and 2500 µg/mL for base/neutral compounds. Prepare the stock surrogate solution by accurately weighing 0.50 ± 0.05 g each of 2-fluorobiphenyl, p-terphenyl-d_{14}, and nitrobenzene-d_5, and 1.00 ± 0.05 g each of 2,4,6-tribromophenol, phenol-d_6, and 2-fluorophenol. Dissolve the materials in methylene chloride and dilute to volume in a 200-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution.

5.8.3 Transfer the stock solution into PTFE-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Stock solutions should be checked regularly for signs of degradation or evaporation, especially just prior to preparing spiking solutions. Allow solutions to come to room temperature before use.

5.8.4 Stock solutions should be replaced after one year, or sooner if analysis indicates a problem.

5.9 Surrogate spiking solution - Prepare a surrogate spiking solution by transferring a 10-mL aliquot of the surrogate stock solution (using a 10-mL volumetric pipet) into a 50-mL volumetric flask containing approximately 20 mL of methylene chloride. Dilute to a final volume of 50 mL with methylene chloride.

5.9.1 Transfer the surrogate spiking solution into PTFE-sealed screw-cap bottles appropriately sized to minimize headspace. Store at 4°C and protect from light. Spiking

solutions should be checked regularly for signs of degradation or evaporation, especially just prior to use.

5.9.2 Surrogate spiking solutions should be replaced after six months, or sooner if analysis indicates a problem.

5.10 Isotopically-labeled analog stock solution - Either surrogates (e.g., the surrogate standards used in Method 8270) or isotopically-labeled analogs of the compounds of interest must be spiked into the Method 0010 train components prior to extraction. Both surrogates and isotopically-labeled analogs may be used, if desired. The use of isotopically-labeled analogs is optional but highly recommended. Common isotopic labels which are used include deuterium and carbon-13; homologs and fluorinated analogs of the compounds of interest may also be used. To assess extraction efficiency, use of an isotopically-labeled analog of the compound of interest is essential. The isotopically-labeled analog is spiked into the matrix immediately prior to extraction, and losses of the spiked compound can be attributed to the sample extraction/concentration process. An isotopically-labeled analog stock solution can be made from pure standard materials or purchased as a certified solution. Even though the use of isotopically-labeled analogs is optional, each compound to be quantitated needs to be represented by a specific recovery standard, whether in the surrogate mixture (Sec. 5.8) or in a separate spike.

5.10.1 Prepare an isotopically-labeled analog stock solution by accurately weighing approximately 0.250 g of each of the materials to be used. Dissolve in methylene chloride and dilute to volume with methylene chloride in a 200-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution.

5.10.2 Transfer the stock solution into PTFE-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Stock solutions should be checked regularly for signs of degradation, evaporation, or isotope exchange, especially just prior to preparing spiking solutions from them. Allow solution to come to room temperature before use.

5.10.3 Stock solutions should be replaced after one year, or sooner if analysis indicates a problem.

5.11 Isotopically-labeled analog spiking solution

5.11.1 Prepare the isotopically-labeled analog standard by transferring a 10-mL aliquot of the stock isotopically-labeled analog stock solution (using a 10-mL volumetric pipet) into a 50-mL volumetric flask containing approximately 20 mL of methylene chloride. Dilute to volume with methylene chloride. The concentration of the spiking solution should allow the isotopically-labeled analogs to be observed in the final sample in approximately the middle of the calibration range for the gas chromatograph/mass spectrometer, assuming 100% recovery.

5.11.2 Transfer the solution into PTFE-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Spiking solutions should be checked regularly for signs of degradation or evaporation, especially just prior to use. Allow solutions to come to room temperature prior to use.

5.11.3 Spiking solutions should be replaced after six months, or sooner if analysis indicates a problem.

5.12 Stock method spike solution - A method spike consists of a spike of a clean matrix (i.e., clean, dry XAD-2®, clean, dry filter, or water) with a solution containing the compounds of interest (the method spike solution). The compound recoveries obtained from a method spike demonstrate that the compounds of interest can be recovered from the matrix, and aid in elucidating the effects of the field matrix. The method spike solution can be made from pure standard materials or purchased as certified solutions. The compounds of interest for the field test should be used as components of the method spike solution. A method spike is generated by spiking clean XAD-2® or clean organic-free reagent water.

5.12.1 Prepare a stock method spike solution by accurately weighing 0.05 g of each of the compounds of interest. Dissolve the materials in methylene chloride and dilute to volume in a 50-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution.

5.12.2 Transfer the stock method spike solution into PTFE-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Stock solutions should be checked regularly for signs of degradation or evaporation, especially just prior to preparing spiking solutions from them.

5.12.3 Stock solutions should be replaced after one year, or sooner if analysis indicates a problem.

5.13 Method spike standard solution

5.13.1 Prepare the method spike standard solution by transferring a 25-mL aliquot of the stock method spike solution (using a 25-mL volumetric pipet) into a 100-mL volumetric flask containing approximately 20 mL of methylene chloride. Dilute to volume with methylene chloride.

5.13.2 Transfer the method spike standard solution into PTFE-lined screw-cap bottles appropriately sized to minimize headspace. Store at 4°C and protect from light. Spiking solutions should be checked regularly for signs of degradation or evaporation, especially just prior to use.

5.13.3 Spiking solutions should be replaced after six months, or sooner if analysis indicates a problem.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 The six components from each Method 0010 sampling train (Figure 1) should be stored at 4°C between the time of sampling and extraction.

6.2 Each sample should be extracted within 14 days of collection and analyzed within 40 days of extraction. The extracted sample should be stored at 4°C.

7.0 PROCEDURE

7.1 The sample preparation procedure for the six parts of the Method 0010 train will result in three sample extracts for analysis:

a) Particulate matter filter and front half rinse;
b) Condensate and condensate rinse; and
c) XAD-2® and condenser/back half rinse.

7.2 Particulate matter filter and front half rinse

7.2.1 Filter - The filter is identified as Container No. 1 in Method 0010.

7.2.1.1 Using clean forceps, place about 10 PTFE boiling chips into the bottom of the round bottom flask of the Soxhlet extractor and connect the Soxhlet extractor to the round bottom flask.

7.2.1.2 Using a clean syringe or volumetric pipet, add a 1-mL aliquot of the surrogate spiking solution (Sec. 5.9) to the filter. If isotopically-labeled analogs are being used, the isotopically-labeled analog solution (Sec. 5.11) may be added at this time. If a method spike is being prepared, the method spike solution (Sec. 5.13) may be added at this time.

7.2.1.2.1 To ensure proper filter spiking, use a volume of approximately 1 mL of spiking solution. Leave the filter in the petri dish, particulate material on top, for spiking. Add the 1 mL of spiking solution uniformly onto the particulate-coated surface of the filter in the petri dish by spotting small volumes at multiple filter locations, using a syringe.

7.2.1.2.2 Repeat the spiking process with isotopically-labeled standards or method spike solution, if these solutions are being used.

7.2.1.3 Using clean forceps, place the particulate matter filter into a glass thimble and position the glass thimble in the Soxhlet extractor, making sure that the filter will be completely submerged in the methylene chloride with each cycle of the Soxhlet extractor. Place a piece of pre-cleaned unsilanized glass wool on top of the filter in the Soxhlet extractor to keep the filter in place. Rinse the petri dish three times with methylene chloride and add rinses to the Soxhlet.

7.2.1.4 The front half rinse (Container No. 2) may contain particulate material which has been removed from the probe. This particulate material should be extracted with the filter.

7.2.1.4.1 To separate particulate matter from the front half rinse, filter the front half rinse. To avoid introducing any contamination, use the same type of filter which has been used in the Method 0010 train, from the same lot as the filter in the Method 0010 train. Filter the Front Half Rinse, rinse Container No. 2 three times with 10-mL aliquots of methylene chloride, and filter the methylene chloride rinses.

7.2.1.4.2 Transfer the filter with any particulate matter to the Soxhlet extractor with the original filter from the Method 0010 train. Extract the two filters together.

7.2.1.4.3 Return the liquid portion of Container No. 2 to its original container for subsequent extraction or, alternatively, the front half rinse can be

filtered directly into a separatory funnel for extraction of the liquid portion of the front half rinse.

7.2.1.5 Slowly add methylene chloride to the Soxhlet extractor containing the two filters through the Soxhlet (with condenser removed), allowing the Soxhlet to cycle. Add sufficient solvent to fill the round bottom flask approximately half full and submerge the thimble containing the filters.

7.2.1.6 Place a heating mantle under the round bottom flask and connect the upper joint of the Soxhlet to a condenser, making sure that the coolant is flowing through the condenser.

7.2.1.7 Allow the sample to extract for 18 hours, adjusting the mantle temperature for cycling (flushing solvent from the Soxhlet into the round bottom flask) approximately once every thirty minutes.

7.2.1.8 After cooling, disconnect the extractor from the condenser. Tilt the Soxhlet slightly until the remaining solvent has drained into the round bottom flask.

7.2.1.9 Transfer the extract from the round bottom flask into a 500-mL amber glass bottle with PTFE-lined screw cap. The bottle should have been rinsed three times each with methanol and methylene chloride. Rinse the round bottom flask three times with approximately 10-mL aliquots of methylene chloride and transfer the rinses to the amber bottle. Store the filter extract at 4°C until extraction of the filtered front half rinse has been completed.

7.2.2 Front half rinse - The front half rinse is identified as Container No. 2 in Method 0010.

7.2.2.1 Transfer the liquid contents of the filtered front half rinse sample to a separatory funnel of appropriate size for the volume of the sample (a typical front half rinse sample is 200 to 300 mL). Rinse the sample container three times with 10-mL aliquots of methylene chloride, transferring the rinses to the separatory funnel after each rinse.

7.2.2.2 Because the front half rinse sample consists of a mixture of methanol and methylene chloride, sufficient organic-free reagent water must be added to the separatory funnel to cause the organic and aqueous/methanol phases to separate into two distinct layers. The methylene chloride layer will be at the bottom of the separatory funnel. Continue to add water until the bottom layer (methylene chloride) does not increase in volume. An increase in volume can be monitored by marking the separatory funnel at the position of the phase separation.

NOTE: The front half rinse is not spiked with any surrogate, isotopic analog, or method spike solutions because the extract from the front half rinse is combined with the extract from the particulate matter filter sample.

7.2.2.3 Add additional methylene chloride, if necessary, so that the ratio of water/methanol to methylene chloride is approximately 3:1. Add sodium hydroxide (Sec. 5.5) until pH of the water layer is > 11 (but < 14). Use wide-range pH paper to determine pH. Shake vigorously for 2 minutes with rapid arm motion, with periodic venting to release excess pressure. Allow the organic layer to separate for at least 10 minutes.

Collect the methylene chloride extract in a 500-mL amber glass bottle with PTFE-lined screw cap, which has been rinsed three times each with methanol and methylene chloride.

7.2.2.4 Add a second volume of methylene chloride (approximately the same volume as the first extraction) to the separatory funnel and repeat the extraction procedure, combining the methylene chloride extracts in the amber bottle.

7.2.2.5 Perform a third extraction in the same manner.

7.2.2.6 Acidify the water to a pH <2 (but > 0) with sulfuric acid (Sec. 5.6) and repeat Sec. 7.2.2.4 three times. Measure pH with wide-range pH paper.

7.2.3 Concentration of filter and front half rinse extracts - The combined extracts and rinses of extract storage bottles will have a total volume of 1 liter or more.

7.2.3.1 Assemble a Kuderna-Danish concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask with clips or springs. Using a clean pair of forceps, place about five PTFE boiling chips into the concentrator tube. If the volume of extract to be concentrated is greater than 500 mL, repeat the concentration as many times as required using the same 500-mL evaporative flask and systematically adding remaining extract (allow to cool slightly before addition of more extract). If repeated concentrations are performed, use new boiling chips each time.

7.2.3.2 Using a clean pair of forceps, place a small portion of precleaned unsilanized glass wool in the bottom of a long stemmed glass funnel (147 mm diameter), and pour a 2.54-cm (1-in) layer of cleaned sodium sulfate (Sec. 5.7) on top of the glass wool (use more sodium sulfate, if possible; fill the funnel to within approximately 1.27 cm (0.5 in) of the top).

7.2.3.3 Rinse the sodium sulfate contained in the funnel three times with methylene chloride; discard the rinses. Support the funnel in a ring or clamp above the flask to prevent tipping.

7.2.3.4 Place the funnel into the upper opening of the K-D flask and slowly pour extracts from the Filter and Front Half Rinse through the sodium sulfate. Rinse the amber jars containing the extracts three times, using approximately 10 mL of methylene chloride each time. Add the rinses to the funnel. Rinse the sodium sulfate with methylene chloride to complete the transfer.

NOTE: During this process, monitor the condition of the sodium sulfate to determine that the bed of sodium sulfate is not solidifying and exceeding its drying capacity. If the sodium sulfate bed can be stirred and is still free-flowing, effective moisture removal from the extracts is occurring. If the sodium sulfate bed has begun to solidify, do not add more extract. Replace the sodium sulfate bed, re-dry the contents of the K-D flask, and continue drying the extracts.

7.2.3.5 Attach a three-ball macro Snyder column to the evaporative flask. Prewet the Snyder column by adding about 2 mL of methylene chloride to the top. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the K-D apparatus, following manufacturer's instructions. Place the K-D

apparatus on a hot water bath (80 - 85°C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 20 to 30 minutes. Rinse sides of K-D during concentration with a small volume of methylene chloride. When the apparent volume of the liquid reaches 6-8 mL, remove the K-D apparatus from the water bath and allow the apparatus to cool and drain for at least 10 minutes.

NOTE: Never let the extract in the concentrator tube go to dryness even though additional solvent is present in the upper portion of the K-D apparatus.

NOTE: If the sample concentration is not completed within the anticipated period of time, check the temperature of the water bath and check the composition of the sample. If the methanol has not been completely removed from the methylene chloride extract by the procedures described in Secs. 7.2.2.2 and 7.2.2.3, residual methanol will concentrate far slower than a methylene chloride extract and analytes will be lost in the concentration step. A sample containing methanol which has been concentrating for a prolonged period of time cannot be recovered, but extracts which contain residual methanol and have not yet been concentrated can be recovered by performing the procedures in Secs. 7.2.2.2 and 7.2.2.3 again.

7.2.3.6 Remove the Snyder column and evaporative flask. With a clean pair of forceps, add two new PTFE boiling chips to the concentrator tube. Attach a two-ball micro Snyder column to the concentrator tube. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the K-D apparatus, following manufacturer's instructions. Prewet the Snyder column with about 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in hot water, supporting the tube with a clamp. When the apparent volume of the liquid reaches 4 - 5 mL, remove the K-D apparatus from the water bath and allow the apparatus to cool and drain for at least 10 minutes. If the volume is greater than 5 mL, add a new boiling chip to the concentrator tube, prewet the Snyder column, and concentrate again on the hot water bath. Wipe moisture from the outside of the concentrator tube. Transfer the extract to a calibrated vial or centrifuge tube, rinse concentrator tube with a minimum volume of methylene chloride and add rinses to the vial, and add methylene chloride, if necessary, to attain a final volume of 5 mL.

Alternatively, the final concentration may be performed by blowing the surface of the solvent with a gentle stream of nitrogen using a glass disposable pipet to direct the stream of nitrogen. When the nitrogen blowdown technique is used, care must be taken to carefully rinse the sides of the vessel using a minimum quantity of methylene chloride to ensure that analytes are in the methylene chloride solution, not deposited on the sides of the glass container. Perform the blowdown procedure in a calibrated vial or centrifuge tube which does not contain boiling chips. The final extract volume must be 5 mL.

7.2.3.7 Transfer the extract to a 10-mL glass storage vial with a PTFE-lined screw cap. Label the extract as Front Half Rinse and Particulate Filter, and store at 4°C until analysis (Sec. 7, Method 8270). Mark the liquid level on the vial with a permanent marker to monitor solvent evaporation during storage.

7.3 Condensate and condensate rinse - The condensate is identified as Container No. 4 in Method 0010; the condensate rinse is Container No. 5.

7.3.1 Transfer the contents of both the condensate and the condensate rinse samples to a clean separatory funnel (expected volume of both containers is approximately 500 mL). Rinse each of the sample containers with three aliquots of methylene chloride (approximately 10 mL each), transferring the rinses to the separatory funnel.

7.3.2 Using a clean syringe or volumetric pipet, add a 1-mL aliquot of the surrogate solution (Sec. 5.9) to the liquid in the separatory funnel. If isotopically-labeled analogs are being used, the isotopically-labeled analog solution (Sec. 5.11) should be added to the separatory funnel.

7.3.3 Perform an initial methylene chloride extraction of the combined condensate/condensate rinse which has been spiked with appropriate spiking solution(s). Add organic-free reagent water as needed to ensure separation of phases. After extraction three times with methylene chloride, check the pH of the condensate/condensate rinse solution with wide-range pH paper.

7.3.3.1 If the solution is acidic (pH < 7), add acid until the pH is < 2 but > 0 and perform another methylene chloride extraction. Then make the condensate/condensate rinse solution basic (pH > 11 but < 14) and perform another methylene chloride extraction. Combine the methylene chloride extracts from all pH levels, remove moisture, and concentrate for analysis.

7.3.3.2 If, after the initial methylene chloride extraction, the condensate/condensate rinse solution is basic, increase pH until the pH is > 11 but < 14, and perform another methylene chloride extraction. Then make the condensate/condensate rinse solution acidic (pH < 2 but > 0) and perform another methylene chloride extraction. Combine the methylene chloride extracts from all pH levels, remove moisture, and concentrate the extract for analysis.

7.3.4 Refer to Sec. 7.2.2.2 and following sections for extraction and concentration of the condensate/condensate rinse extract.

7.4 XAD-2® - The sorbent trap section of the organic module is identified as Container No. 3 in Method 0010. The sorbent trap section of the organic module shall be used as a sample transport container.

7.4.1 Using clean forceps, place about 10 PTFE boiling chips in the bottom of the round bottom flask of the Soxhlet extractor and connect the Soxhlet extractor to the round bottom flask.

7.4.2 Transfer the XAD-2® to the extraction thimble. Remove the glass wool plug from the XAD-2® trap and add to the thimble of the Soxhlet extractor. If ground glass stoppers are used to seal the sorbent trap during shipment, these ground glass stoppers should be rinsed with methylene chloride and the rinsate added to the round bottom flask of the Soxhlet extractor.

7.4.2.1 If the XAD-2® is dry (i.e., free-flowing), pour the XAD-2® directly into the thimble (or directly into the Soxhlet extractor) and rinse the trap with methylene chloride, adding the rinses to the round bottom flask.

7.4.2.2 If the XAD-2® is wet, removal from the trap may be difficult. To accomplish the transfer, flush the resin from the trap using a PTFE wash bottle containing methylene chloride. Alternatively, acidic water (pH < 2) can be used to wash the walls of the XAD-2® trap. Collect the resin and solvent in a clean 500-mL beaker. Transfer the XAD-2®/methylene chloride from the beaker to the extraction thimble, taking care that no solvent is lost. Alternatively, the XAD-2® can be transferred directly to the Soxhlet extractor and the methylene chloride rinse and transfer solvent allowed to drain through the XAD-2® to the round bottom flask. Rinse the beaker several times with methylene chloride, pouring the rinses through the XAD-2® bed once the extraction thimble is in the Soxhlet extractor. Be sure that a glass wool plug is in place above the XAD-2® to ensure that the XAD-2® does not float out of the thimble.

NOTE: Under no circumstances should methanol or acetone be used to transfer the resin.

7.4.2.3 Alternative approaches to transfer of XAD-2® from the trap to the extraction thimble are discussed below.

7.4.2.3.1 The XAD-2® can be transferred directly to the Soxhlet extractor and the methylene chloride rinse and transfer solvent allowed to drain through the XAD-2® to the round bottom flask. If ground glass stoppers are used to seal the sorbent trap during shipment, these ground glass stoppers should be rinsed with methylene chloride and the rinsate added to the round bottom flask of the Soxhlet extractor. To remove the XAD-2® from the sampling module, remove the glass wool from the end of the XAD-2® sampling module. Place this glass wool in the Soxhlet extractor to ensure thorough extraction of the glass wool. If the XAD-2® is being transferred directly to the Soxhlet extractor, place a small piece of pre-cleaned glass wool in the side-arm of the Soxhlet extractor to ensure that no XAD-2® enters the side-arm of the Soxhlet extractor. Invert the XAD-2® sampling module (glass frit up) over an extraction thimble contained in a beaker, or directly over the Soxhlet extractor with pre-cleaned glass wool in the bottom, as shown in Figure 2. Add approximately 5 to 10 mL of methylene chloride above the glass frit of the sampling module. Connect a rubber pipet filler bulb with check valve that has been fitted with a ball joint to the XAD-2® sampling module. Using air pressure created by squeezing the bulb, gently but firmly push the methylene chloride through the frit, forcing the XAD-2® out of the sampling module. Avoid allowing methylene chloride to be pulled up into the bulb, since the sample will be compromised if methylene chloride is pulled up into the bulb and allowed to become part of the extract. This process will need to be repeated 3 to 5 times. Use a PTFE wash bottle containing methylene chloride to rinse the walls of the sampling module to transfer XAD-2® which has been retained on the walls of the sampling module after transfer of XAD-2® to the Soxhlet. A methylene chloride rinse of the walls will not remove all of the XAD-2®, but after 3 to 5 rinses of the walls of the sampling module, no more than a monolayer of XAD-2® particles should be retained. If more than a monolayer of XAD-2® remains, additional rinses are required. The glass wool in the side arm of the Soxhlet extractor must be removed and added to the Soxhlet.

NOTE: Under no conditions should methanol or acetone be used in the transfer of the XAD-2®.

7.4.2.3.2 Alternatively, the wet XAD-2® may be transferred from the sampling module to a piece of cleaned aluminum foil by inverting the trap (glass frit up) and tapping the trap on a solid surface covered with the cleaned aluminum foil. This process is slow and may result in breakage of the sampling module. If ground glass stoppers are used to seal the sorbent trap during shipment, these ground glass stoppers should be rinsed with methylene chloride and the rinsate added to the round bottom flask of the Soxhlet extractor. After the majority of the XAD-2® has been removed from the trap by tapping, the XAD-2® on the aluminum foil may be transferred to the extraction thimble. The sampling module should be rinsed with methylene chloride to flush the remaining XAD-2® particles adhering to the glass wall into the extraction thimble. After all XAD-2® has been transferred into the Soxhlet thimble, add a plug of glass wool to the top of the XAD-2® to hold the resin in place.

7.4.3 With the XAD-2® in the Soxhlet extractor and glass wool on top of the XAD-2®, use a clean syringe or volumetric pipet to add a 1-mL aliquot of the surrogate spiking solution to the XAD-2®. Be sure that the needle of the syringe penetrates the XAD-2® bed to a depth of at least 1.27 cm (0.5 in). If isotopically-labeled standard solution or method spike solution is being used, these solutions should be spiked at this time.

7.4.4 Container No. 5 contains the methylene chloride/methanol rinse of the condenser and all train components from the back half of the filter holder to the XAD-2® sampling module. These rinses consist of 50:50 methanol:methylene chloride. Transfer the contents of Container No. 5 to a separatory funnel and rinse the container with three 10-mL aliquots of methylene chloride. Add the rinses to the separatory funnel. Sufficient organic-free reagent water must be added to the separatory funnel to cause the organic and aqueous phases to separate into two distinct layers. Refer to Sec. 7.2.2.2 and following sections for preparation of a methylene chloride extract from Container No. 5. Add the methylene chloride layer from the separatory funnel directly to the Soxhlet extractor containing the XAD-2® or collect the methylene chloride extract in a container and transfer from this container to the Soxhlet containing the XAD-2®. Pour the methylene chloride extract of the condenser and back half rinses through the XAD-2® in the Soxhlet extractor; rinse the container or separatory funnel 3 times with approximately 10-mL aliquots of methylene chloride and add the rinses to the Soxhlet.

7.4.5 Add additional methylene chloride to the Soxhlet extractor, if necessary, pouring approximately 300-400 mL through the XAD-2® bed so that the round bottom flask is approximately half-full and the XAD-2® bed is covered.

7.4.6 Place a heating mantle under the round bottom flask and connect the upper joint of the Soxhlet extractor to a condenser.

NOTE: Start the extraction process immediately after surrogate/analog spiking is completed to ensure that no volatilization of organic compounds from the resin or any spiking solutions occurs before the extraction process is started.

7.4.7 Allow the sample to extract for at least 18 hours but not more than 24 hours, cycling once every 25 - 30 minutes.

NOTE: Be sure that cooling water for the condensers is cold and circulating. Watch the extractor through two or three cycles to ensure that the extractor is working properly.

7.4.8 After the Soxhlet extractor has been cooled, disconnect the extractor from the condenser and tilt the extractor slightly until the remaining solvent in the Soxhlet has drained into the round bottom flask.

7.4.9 Inspect the contents of the round bottom flask to determine whether there is a visible water layer on top of the methylene chloride. If no water layer is observed, transfer the extract into a 500-mL amber glass bottle with PTFE-lined screw cap for storage (Sec. 7.2.1.8), or proceed directly with removal of moisture and concentration of the extract (Sec. 7.2.3.1). If a water layer is observed in the Soxhlet round bottom flask, transfer the contents to a separatory funnel, rinsing the round bottom flask three times with methylene chloride and adding the rinsings to the separatory funnel. Drain the methylene chloride from the separatory funnel and store in an amber glass bottle. Then perform an acid/base extraction of the water layer remaining in the separatory funnel (Sec. 7.3.3). Add the methylene chloride extract from the acid/base extraction to the methylene chloride extract from the round bottom flask in the amber glass jar. Store the extract in the amber glass bottle at 4°C for subsequent removal of moisture and concentration following the steps outlined in Sec. 7.2.3.1.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific Quality Control procedures.

8.2 A method blank consists of a clean filter, clean dry XAD-2®, or organic-free reagent water, which is spiked with surrogates prior to extraction. The method blank is extracted and concentrated using the same procedures as the corresponding sample matrix. One method blank is extracted and analyzed for every ten samples.

8.3 A method spike consists of a clean filter, XAD-2®, or organic-free reagent water, which is spiked with surrogates, isotopically-labeled standards, if used, and method spike solution, if used, prior to extraction. The method spike is extracted and concentrated using the same procedures as the corresponding sample matrix. At least one method spike is extracted and analyzed for every matrix, with a frequency of one method spike for every twenty samples.

9.0 METHOD PERFORMANCE

9.1 Method Performance Evaluation - Evaluation of analytical procedures for a selected series of compounds must include the sample preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through all the procedures.

9.2 Method Detection Limits - The overall method detection limits (lower and upper) need to be determined on a compound-by-compound basis because different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrument minimum detection limits. The method detection limit needs to be quoted relative to a given sample volume. The upper limits for the method need to be determined relative to compound retention volumes (breakthrough).

9.3 Method Precision and Bias - The overall method precision and bias needs to be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and

extraction efficiency of the train components. The surrogate recoveries shown below represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

10.0 REFERENCES

1. Bursey, J., Homolya, J., McAllister, R., and McGaughey, J., Laboratory and Field Evaluation of the SemiVOST Method, Vols. 1 and 2, U. S. Environmental Protection Agency, EPA/600/4-851/075A, 075B. 1985.

2. Handbook. Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration, EPA-625/6-89-023, Cincinnati, OH. 1990.

3. Bursey, J., Merrill, R., McAllister, R., and McGaughey, J., Laboratory Validation of VOST and SemiVOST for Halogenated Hydrocarbons from the Clean Air Act Amendments List, Vols. 1 and 2, U. S. Environmental Protection Agency, EPA 600/R-93/123a and b, (NTIS PB93-227163 and PB93-227171) Research Triangle Park, NC. July. 1993.

4. McGaughey, J., Bursey, J., and Merrill, R., Field Test of a Generic Method for Halogenated Hydrocarbons, U. S. Environmental Protection Agency, EPA 600/R-93/101, (NTIS PB 93-212181), Research Triangle Park, NC. July, 1993.

TABLE 1

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	Relative Standard Deviation (%)
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate recovery values shown in Table 1 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

FIGURE 1

METHOD 0010 SAMPLING TRAIN

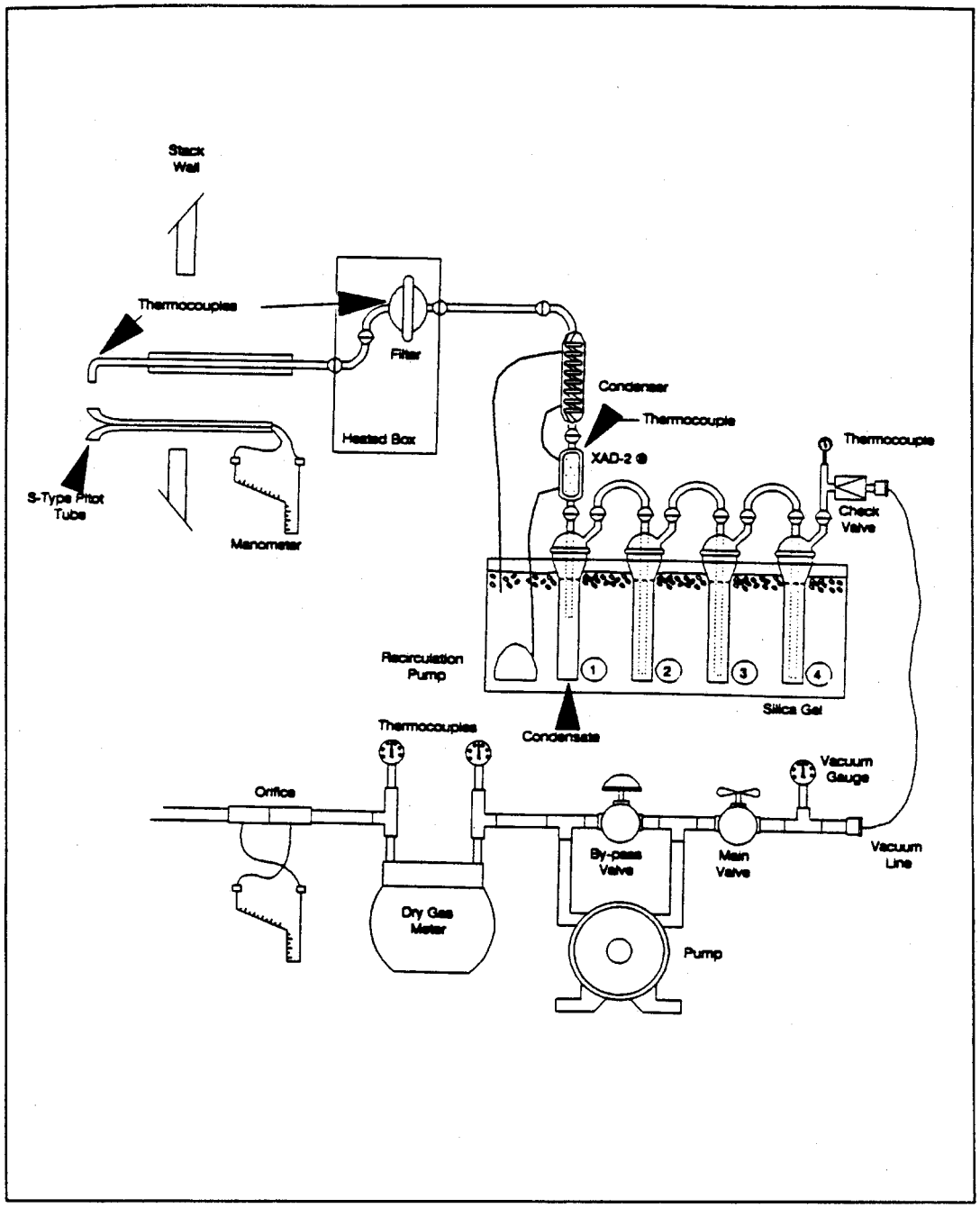

FIGURE 2

TRANSFER OF WET XAD-2®

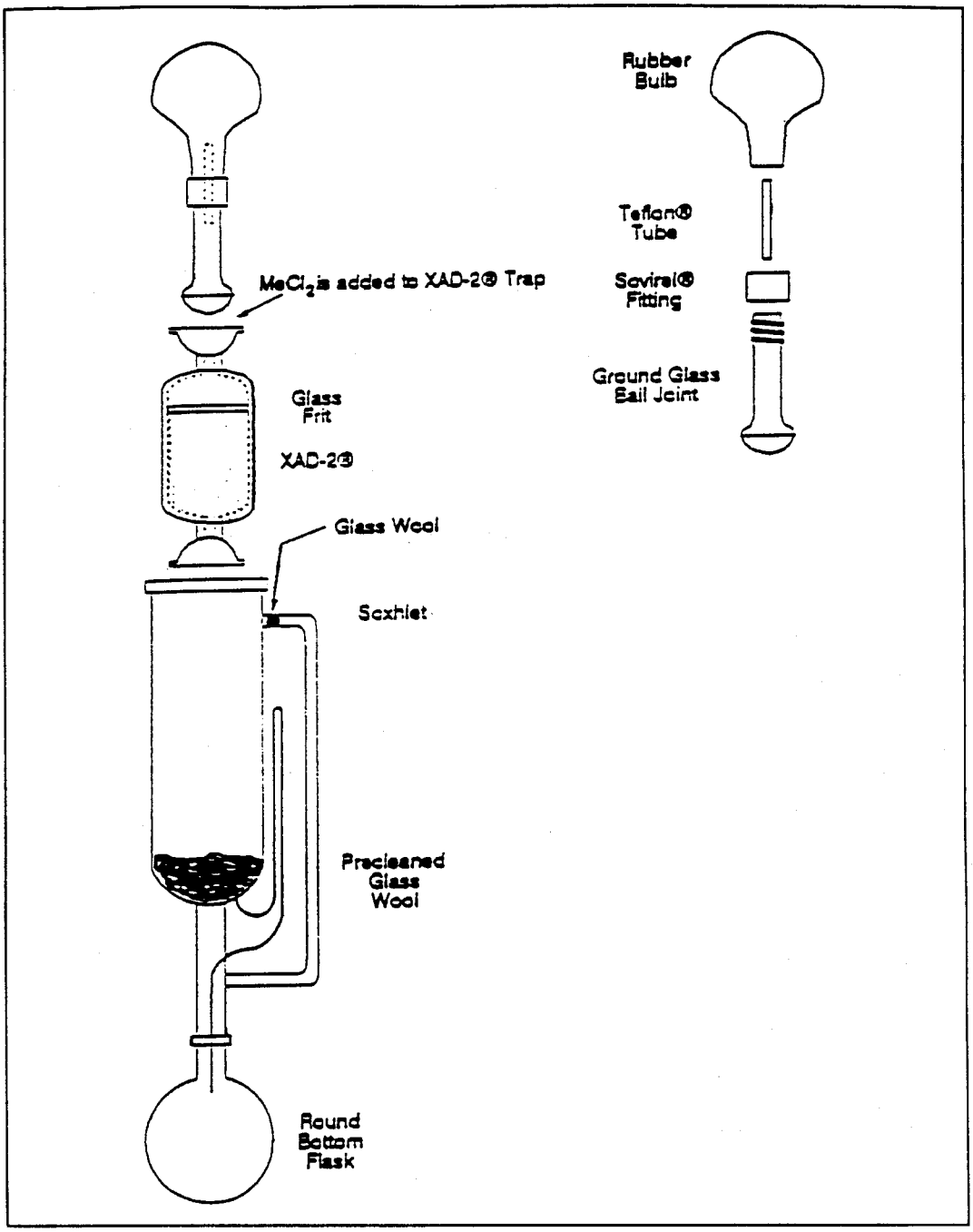

FIGURE 3

SAMPLE PREPARATION FLOWCHART USING METHOD 0010
(MODIFIED METHOD 5) SAMPLING TRAIN

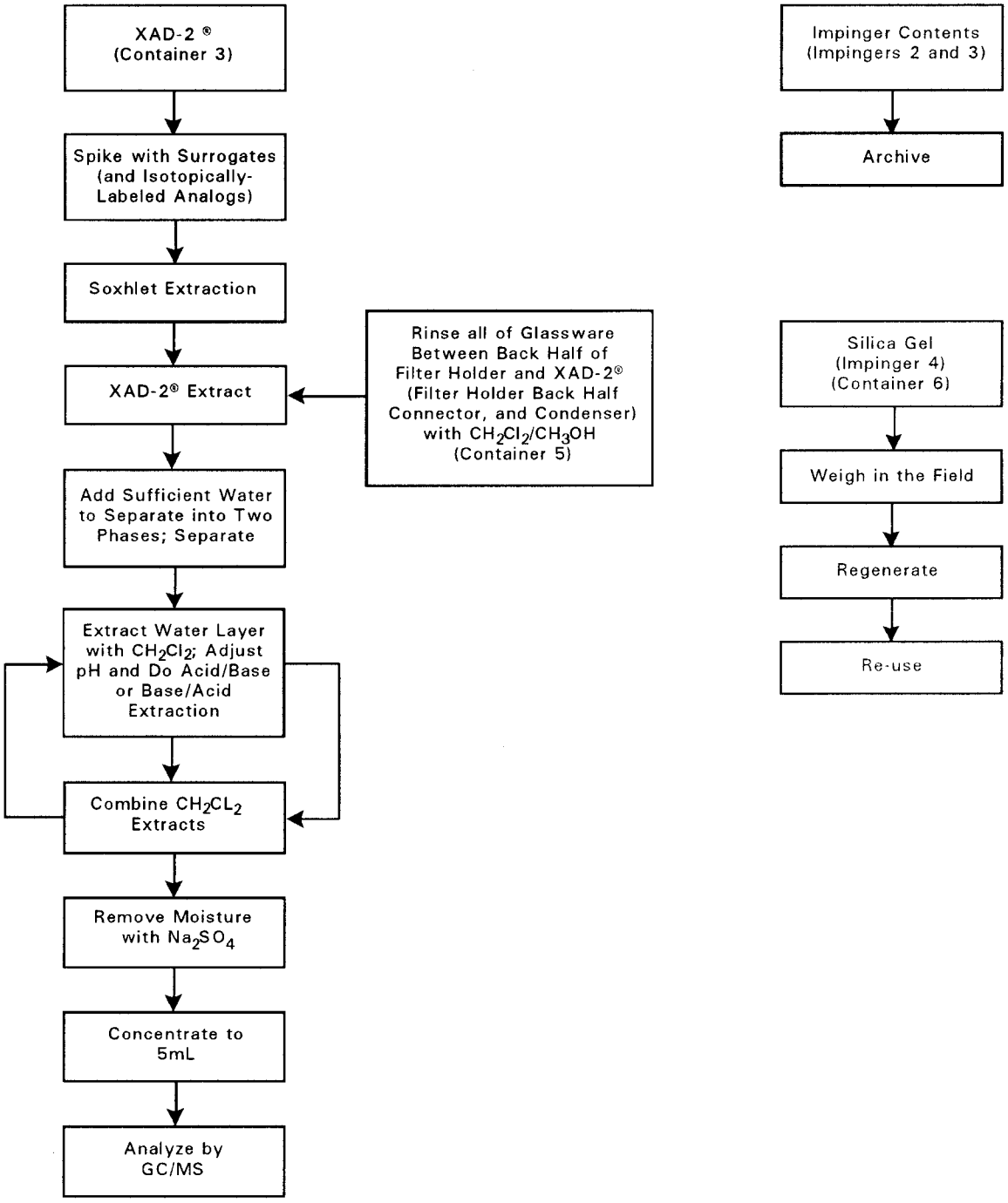

FIGURE 3 (continued)

SAMPLE PREPARATION FLOWCHART USING METHOD 0010
(MODIFIED METHOD 5 SAMPLING TRAIN)