SUPERCRITICAL FLUID EXTRACTION OF POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 3561 describes the use of supercritical fluids for the extraction of polynuclear aromatic hydrocarbons (PAHs) from soils, sediments, fly ash, solid-phase extraction media, and other solid materials which are amenable to extraction with conventional solvents. This method is suitable for use with any supercritical fluid extraction (SFE) system that allows extraction conditions (e.g., pressure, temperature, flow rate) to be adjusted to achieve extraction of the PAHs from the matrices of concern. The following compounds may be determined by this method:

Compound	CAS No[a]
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benz(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(g,h,i)perylene	191-24-2
Benzo(a)pyrene	50-32-8
Chrysene	218-01-9
Dibenz(a,h)anthracene	53-70-3
Fluoranthene	206-44-0
Fluorene	86-73-7
Indeno(1,2,3-cd)pyrene	193-39-5
Naphthalene	91-20-3
Phenanthrene	85-01-8
Pyrene	129-00-0

[a] Chemical Abstract Service Registry Number

1.2 Method 3561 is not suitable for the extraction of PAHs from liquid samples without some treatment of the liquid prior to introduction into the SFE system. If liquid samples are not first "stabilized," the sample may be extruded through the end pieces of the SFE device without undergoing extraction. In the case of aqueous samples, one approach is to use solid-phase extraction (SPE), as described in Method 3535. The aqueous sample may be passed through an SPE disk and the analytes extracted from the disk using SFE.

1.3 The extraction conditions listed in this procedure (Sec. 7.5) were used to develop the data using a variable restrictor and solid trapping media referenced in Sec. 9.2. Other extraction conditions and equipment are acceptable as long as appropriate method performance is demonstrated. The method performance demonstration should be based on the extraction of a certified sample, not on spiked soil/solids. Alternatively, a comparison of SFE and Soxhlet extraction data using an environmentally contaminated PAH sample may be performed. Follow the guidance

for the initial demonstration of laboratory proficiency found in Section 8.0 of Method 3500, but utilize a weathered sample instead of a spiked sample.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The method is divided into three discrete steps. The extraction conditions for the first two steps are designed to ensure the best recovery for the range of volatilities found among the PAHs. The third step is used as a final sweep of modifier within the system. It should be noted that the separation of the PAHs into the two arbitrary classes of the "more volatile PAHs" (step 1) and the "lesser volatile PAHs" (step 2) is not a clean separation of compounds, but a rough group separation depending upon the actual compounds and their relative abundance in the sample matrix. The net sum of the two groups is recombined in the end and thus empirically does not depend upon a discrete definition or naming of the compounds in each group.

2.1.1 Step 1 - The more volatile PAHs are extracted and recovered in this step using pure CO_2 at moderately low density and temperature and with cold trapping on an ODS trap. These PAHs are reconstituted into an autosampler vial with 0.8 mL collected fraction volume.

2.1.2 Step 2 - The lesser volatile PAHs are removed in this step using a mixture of CO_2 with water and methanol as the extraction fluid, higher operating temperature and density in the extraction region, and a higher temperature in the trapping region with the ODS. The PAHs are not reconstituted directly after the second step.

2.1.3 Step 3 - A short third step with pure CO_2 (but with all other conditions as in the second step) is used to purge the system of modifier before depressurization. The analytes recovered in the second step (and possibly, any moved during the beginning of the third step) are reconstituted in the same autosampler vial containing the first fraction, using another 0.8-mL collected fraction volume. Therefore, all recovered analytes are merged automatically into a single fraction to be analyzed by HPLC.

2.2 There are also optional extraction solvents and SFE extraction conditions provided that are more amenable to GC and GC/MS analysis.

3.0 INTERFERENCES

3.1 The analyst must demonstrate through the analysis of reagent blanks (collection solvent treated as per Sec. 7.4) that the supercritical fluid extraction system is free from interferants. To do this, perform a simulated extraction using an empty extraction vessel and a known amount of carbon dioxide under the same conditions as those used for sample extraction, and determine the background contamination by analyzing the extract by the appropriate determinative method.

3.2 The extraction vessel(s), the end-frits, the nozzle [restrictor(s)], and the multi-port valve(s) may retain solutes whenever high-concentration samples are extracted. It is, therefore, good practice to clean the extraction system after such extractions. Replacement of suspected parts of the system should be done when reagent blanks indicate carryover. At least one reagent blank should be prepared and analyzed daily when the instrument is in use. Furthermore, reagent blanks should be prepared and analyzed after each extraction of a high-concentration sample (high part per

million or mg/kg range). If reagent blanks continue to indicate contamination, even after replacement of the extraction vessel (and the restrictor, if a fixed restrictor system is used), the multi-port valve must be cleaned. The operator must be ever vigilant against impurities arising from liquid solvents and carbon dioxide itself. Avoid any apparatus, valves, solenoids, and other hardware that contain lubricants, and chlorofluorohydrocarbon materials that can serve as background contaminant sources.

3.3 When using modifiers, it is important to consider that the modifiers at collection regions that are colder than the boiling point of the modifier(s) may cause some modifier condensation in that region. Depending upon the specific design of the instrumentation and the quantities of modifiers used within a step, there is a potential problem of flooding the collection region and thereby losing the analytes of interest. With SFE instrumentation employing solid (packed) traps for the collection and concentration of the extracted components, a convenient guideline is to think of the trap as a packed GC column during the extraction step (the CO_2 and any modifiers are the gaseous mobile phase) and as a packed LC column during the reconstitution step. Therefore, migration during the "GC-column-like" operation should be minimized by the selection of various parameters: trap temperature, chemical activity of the packing, expended flow rates, and extraction times (how long the migration has to proceed). Migration during the "LC-column-like" operation should be controlled to trade-off band-broadening with elution time through the use of reconstitution solvent flow rate and composition and the trap temperature during reconstitution.

3.4 Refer to Method 3500, Sec. 3.0, for general extraction interference guidance.

4.0 APPARATUS AND MATERIALS

4.1 Supercritical fluid extractor and associated hardware - Any supercritical fluid extraction system that can achieve the extraction conditions and performance specifications detailed in this procedure may be used.

Figure 1 depicts a typical supercritical fluid extractor system, including a carbon dioxide source, a pumping system (liquid carbon dioxide), an extraction thimble, a restriction device, and analyte collection device, temperature control systems for several zones, and an overall system controller. The lower left-hand side of Figure 1 depicts a cylinder of liquid carbon dioxide, which is the extractant fluid. The carbon dioxide is provided as a liquid-gas mixture. Because the liquid is the more dense of the two phases, it is drawn from the bottom of the tank with an eductor tube. It is essential that a full-length eductor tube is installed in the cylinder, regardless of the grade of carbon dioxide used. The carbon dioxide remains a liquid throughout the pumping or compression zones, and passes through small-diameter metal tubing as it approaches the extraction thimble. Some systems may include a preheating zone in front of the extraction zone, so that supercritical temperature, pressure, and density conditions are applied immediately to the analyte matrix in the thimble. Analytes are collected just beyond the exit end of the restrictor, either 1) on an impinged surface, such as a small, packed trap, or 2) in an empty vial or a vial containing an appropriate liquid.

WARNING: A safety feature to prevent over-pressurization is required on the extractor. This feature should be designed to protect the laboratory personnel and the instrument from possible injuries or damage resulting from equipment failure under high pressure.

4.1.1 Extraction vessel - Use the extraction vessel supplied by the manufacturer of the SFE system being used. The vessels may be constructed of stainless steel, polyether ether ketone (PEEK), or other suitable materials. Both the extraction vessel and the fittings used

for the vessel must be capable of safely withstanding the necessary extraction pressures, which range as high as 4900 psi (see Sec. 7.5). Check with the manufacturer of the particular extraction system for the maximum operating pressure and temperature of the system, as some vessels and fittings may not be capable of performing all of the extractions described in this method at the specified extraction pressures and temperatures.

4.1.2 Restrictor - This method was developed using continuously variable nozzle restrictors. Such restrictors have been found to be less likely than fixed nozzle restrictors to become plugged with ice derived from moisture in the sample. In addition, the recommended extraction fluids for some analytes to be analyzed via HPLC include mixtures of carbon dioxide, organic solvents, and water. Therefore, if other restrictors (e.g., tapered restrictors, static pinhole restrictors, frit restrictors, variable orifice restrictors, crimped metal tubing, or PEEK tubing) are employed, the analyst must demonstrate that the extraction and collection conditions described here (or modified by the laboratory) are appropriate for the analytes of interest in the matrix of interest. Such demonstrations are described in general in Method 8000, Sec. 8.

4.1.3 Collection device - This method is based on a solid trap used at both sub-ambient and above ambient temperatures for different sub-sets of the method. However, data are also presented on the use of a liquid trap (see Sec. 9.0).

4.1.3.1 When the analytes are collected in solvent, care must be taken in validation of the method, particularly for the first eight PAH compounds (Method 8310 elution order) which are often poorly recovered in liquid traps. The use of a glass wool plug in the inner tube of the collection vial improves recoveries. Flow must not be so high as to reduce the collection solvent to dryness. A 15-mL collection solvent volume is recommended.

4.1.3.2 When the analytes are trapped on a sorbent material, use ODS (Hypersil ODS was used to develop the method performance data for the solid sorbent trap), 30-40 micrometer particle diameter commonly used in solid phase extraction (SPE) cartridges. Other trapping materials have also been found to provide acceptable results, e.g. diol, however, if other material is used it should demonstrate equivalent trapping efficiency to the ODS.

4.2 Carbon dioxide cylinder balance (optional) - Balances from White Associates, Catalog No. 30, or Scott Specialty Gases Model 5588D, or equivalent, can be used to monitor the fluid usage. Such a device is useful because carbon dioxide tanks used for SFE are not equipped with regulators. This makes it difficult to determine when the tank needs to be replaced.

4.3 Filter paper disks to be placed at both ends of the sample. Disks may be cored from Whatman Qualitative filter paper, Catalog No. 1003-055, or equivalent; or from Baxter glass fiber filter paper, 0.5 µm, Catalog No. F232, 2-21, or equivalent.

5.0 REAGENTS

5.1 Carbon dioxide, CO_2 - Either supercritical fluid chromatography (SFC)- or SFE-grade CO_2 may be acceptable for use in SFE. However, SFC-grade CO_2 may contain more impurities then SFE-grade, and therefore may be unsuitable for trace analysis. Aluminum cylinders are generally preferred over steel cylinders. Depending on the specific instrumentation, the cylinders may need to be fitted with eductor tubes and the contents pressurized under 1500 psi of helium head pressure.

Consult the SFE system manufacturer's instructions regarding the specific cylinder configuration required.

5.2 Carbon dioxide (CO_2) for cryogenic cooling - Certain parts of some models of extractors (i.e., the high-pressure pump head and the analyte trap) must be cooled during use. The carbon dioxide used for this purpose must be dry, and should be supplied in tanks with full-length eductor tubes.

5.3 Modifiers (also called co-solvents) were added to the bulk CO_2 extraction fluid through the use of a separate (stand-alone) HPLC pump with the output joined in a TEE-piece to the flowing carbon dioxide stream after the carbon dioxide pump but before the extraction vessel. The modifier solvents are methanol, water, and methylene chloride (HPLC grade), forming extraction fluid mixtures of 95/1/4 (v/v/v) CO_2/methanol/water for HPLC analysis and 95/1/4 (v/v/v) CO_2/methanol/methylene chloride in the case where GC or GC/MS was used for the analytical measurement. There are concerns about the 4% water modifier leaving residual water in the collection trap that could have a detrimental effect on the gas chromatographic separation. Hence, the extraction fluid composition of 95/1/4 (v/v/v) CO_2/water/methanol should be altered to 95/1/4 (v/v/v) CO_2/methylene chloride/methanol - with some of the other parameters in the SFE method modified slightly as described in Section 7.0.

5.4 Reconstitution solvents - The reconstitution solvents dispensed by the SFE instruments using solid phase trapping may be the same material used for liquid trapping. This method was developed only with sub-ambient solid trapping. These same solvents were used to prepare the internal and external standard solutions. A 50/50 (v/v) mixture of acetonitrile/tetrahydrofuran (THF) was used when HPLC analysis was chosen: both were HPLC grade. A 75/25 (v/v) mixture of methylene chloride/isooctane was used when GC/MS was chosen for the analytical measurement. In addition, data from a different laboratory using a liquid trap are referenced in Sec. 9.3.

5.5 Surrogates - Recommended surrogates are bromobenzene (early eluter) and *p*-quaterphenyl (late eluter available from ChemService, West Chester, PA). Prepare a stock solution at a concentration of 10 g/L in a 50/50 (v/v) acetonitrile/THF mixture. Apply 150-µL aliquots to the soil samples within the extraction vessels at the exit end of the flow-through vessels. It has been observed that very small volumes (10 µL) of a concentrated surrogate mixture (100-1000 g/L) often gave poor recoveries while adding larger volumes of more dilute surrogate solution to the sample matrix achieved the expected recoveries.

5.6 Copper powder (electrolytic grade) - Added to samples which contain elemental sulfur. It is pretreated by sequentially rinsing 20 g with 150 mL of organic-free reagent water, 150 mL of acetone, 150 mL of hexane, and then drying in a rotary evaporator. The powder is then kept under argon until used. Copper powder must have a shiny bright appearance to be effective. If it has oxidized and turned dark it should not be used.

5.7 Sodium sulfate, anhydrous (12-60 mesh), Baker Analyzed or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Solid samples for this procedure should be collected and stored as any other solid samples containing semivolatile organics.

7.0 PROCEDURE

7.1 Sample handling - Decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially composited samples. Discard any foreign objects such as pieces of wood, glass, sticks, leaves and rocks.

7.2 Determination of sample % dry weight - In certain cases, sample results are desired based on dry-weight basis. When such data are desired, a separate portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination. Also, a moisture content in the sample between 10 - 50% for the GC/MS extraction method, provided the best extraction efficiency for the procedure as written. Therefore, determination of % moisture is necessary in this case.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.2.1 Immediately after weighing the sample for extraction, weigh an additional 5 - 10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

7.2.2 Calculate the % dry weight as follows:

$$\%\ \text{dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Safety considerations - Read Sec. 11.0, "Safety", before attempting to perform this procedure.

7.4 Sample grinding and homogenization.

NOTE: Sample grinding is a critical step in the SFE process. The soil/solid must be ground to a fine particle to ensure efficient extraction.

7.4.1 Mix at least 100 grams of sample with an equal volume of carbon dioxide solid "snow" prepared from the extraction grade carbon dioxide. Place this in a small food-type chopper, and grind for about one minute. Place the chopped sample on a clean surface and allow the carbon dioxide to sublime away. As soon as the sample appears free-flowing and without the solid carbon dioxide, weigh the sample and place in the extraction vessel. This procedure will ensure the homogeneity of the sample without loss of the volatile analytes and also retains the original moisture content of the sample.

7.4.2 Weigh 2.0 to 3.0 g of the homogenized sample into a pre-cleaned aluminum dish. (Up to 10 g of sample can be extracted using the conditions outlined in this procedure.) If sample moisture content exceeds 50%, add a plug (1 - 2 g) of anhydrous sodium sulfate (Sec. 5.7) next to the downstream frit in the extraction vessel. Do not add any drying agent of any kind directly to the sample. This method depends upon the controlled addition of water throughout the procedure. Any drying agents will interfere with the process.

7.4.3 For samples known to contain elemental sulfur, use copper powder (electrolytic grade) to remove the dissolved sulfur from the sample and carbon dioxide eluant. The copper powder (1 to 2 grams per sample) can be packed in a separate vessel between the extraction vessel and the nozzle (restrictor) or better, mixed with the sample in the extraction vessel itself.

Alternatively, a plug of copper powder may be placed in the extraction vessel beyond the sample before the exit-frits.

7.4.4 Transfer half of the weighed sample to the extraction vessel. Add 150 µL of surrogate solution to the sample in the vessel and then add the remainder of the sample material. To ensure efficient extraction, it is very important that the extraction vessel be completely full to avoid any dead volume. If any dead volume exists, fill the space with an inert, porous material, e.g., pre-cleaned Pyrex® glass wool, Celite®, etc.

7.5 Sample extraction - This section contains recommended extraction parameters for both HPLC and GC (including GC/MS) analyses.

NOTE: The CO_2/modifiers used for GC or GC/MS analysis extract more efficiently when the soil moisture content is between 10 to 50%. If the sample content is less than 10%, add 0.5 mL of water per gram of sample to the sample before placing it in the extraction vessel.

7.5.1 The following conditions for Step 1 (collection of the more volatile PAHs) are grouped according to function.

7.5.1.1 Extraction

Pressure:	1750 psi (120 bar)
Density:	0.30 g/mL
Extraction chamber temperature:	80°C
Extraction fluid composition:	CO_2
Static equilibration time:	10 minutes
Dynamic extraction time:	10 minutes
Extraction fluid flow rate:	2.0 mL/min

Resultant thimble-volumes-swept = 9.1 (this is equivalent to 20 mL of liquid carbon dioxide at a reference temperature of 4.0°C, density 0.96 g/mL or 19.2 g of carbon dioxide).

7.5.1.2 Collection (during extraction)

Trap packing:	ODS
Trap temperature:	-5°C
Nozzle temperature:	80°C (variable restrictor)

7.5.1.3 Reconstitution (of collected extracts)

Rinse solvent for HPLC:	50/50 (v/v) THF/acetonitrile
Rinse solvent for GC:	75/25 (v/v) CH_2Cl_2/isooctane
Collected fraction volume:	0.8 mL
Trap temperature:	60°C
Nozzle temperature:	45°C (variable restrictor)
Rinse solvent flow rate:	1.0 mL/min

The extract should be properly labeled with fraction designation and vial number.

7.5.2 The following conditions for Step 2 (collection of the lesser volatile PAHs) are grouped according to function.

7.5.2.1 Extraction

Pressure:	4900 psi (338 bar)
Density:	0.63 g/mL
Extraction chamber temperature:	120°C
Extraction fluid for HPLC:	95/1/4 (v/v/v) CO_2/methanol/water
Extraction fluid for GC:	95/1/4 (v/v/v) CO_2/methanol/CH_2Cl_2
Static equilibration time:	10 minutes
Dynamic extraction time:	30 minutes
Extraction fluid flow rate:	4.0 mL/min

Resultant thimble-volumes-swept = 25 (equivalent to 120 mL of liquid carbon dioxide at reference temperature of 4.0°C, density 1.06 g/mL or 127 g of carbon dioxide).

7.5.2.2 Collection (during Extraction)

Trap packing:	ODS
Trap temperature:	80°C
Nozzle temperature:	80°C (variable restrictor)

7.5.2.3 Reconstitution (of collected extracts) - none.

7.5.3 The following conditions for Step 3 (final sweep of modifiers) are grouped according to function.

7.5.3.1 Extraction

Pressure:	4900 psi (338 bar)
Density:	0.63 g/mL
Extraction chamber temperature:	120°C
Extraction fluid composition:	CO_2
Static equilibration time:	5 minutes
Dynamic extraction time:	10 minutes
$C0_2$ flow rate:	4.0 mL/min

Resultant thimble-volumes-swept = 8 (equivalent to 40 mL of liquid carbon dioxide at reference temperature of 4.0°C, density 1.06 g/mL or 42.4 g carbon dioxide).

7.5.3.2 Collection (during Extraction)

Trap packing:	ODS
Trap temperature:	80°C
Nozzle temperature:	80°C (variable restrictor)

NOTE: All three steps consume a total of 188.6 g of carbon dioxide.

7.5.3.3 Reconstitution (of collected extracts)

Rinse solvent for HPLC:	50/50 (v/v) THF/acetonitrile
Rinse solvent for GC:	75/25 (v/v) CH_2Cl_2/isooctane
Collected fraction volume:	0.8 mL
Trap temperature for HPLC:	80°C
Trap temperature for GC:	60°C
Nozzle temperature:	45°C (variable restrictor)
Rinse solvent flow rate:	1.0 mL/min

The extract should be properly labeled with fraction destination and vial number.

7.5.4 The combined extract volumes consist of 1.6 mL. The extract is ready for the analysis by Methods 8310 (HPLC), 8270 (GC/MS), or 8100 (GC/FID). Note that there are no performance data available on the analysis of SFE PAH extracts by Method 8100. Furthermore, the procedure is more susceptible to interferences in complex samples.

NOTE: If a fixed restrictor and liquid trapping are used, a restrictor temperature in the range of 100 to 150°C is recommended.

7.5.5 When GC or GC/MS analysis procedures are to be used and sulfur interference becomes apparent at time of analysis, Method 3660 may be used to remove the sulfur from the extract.

7.6 SFE System Maintenance

7.6.1 Depressurize the system following the manufacturer's instructions.

7.6.2 After extraction of an especially "tarry" sample, the end-frits of the extraction vessel may require replacement if not extensive cleanup to ensure adequate extraction fluid flow without excessive pressure drop due to the system plumbing. In addition, very fine particles may clog the exit frit requiring its replacement. By placing a layer of inert material such as Celite® or sea sand above the sample prior to the exit frit (and placing disks of filter paper on top of the inert material), this maintenance may be delayed for some period of operation.

7.6.3 Clean the extraction vessel after each extraction sample. The cleaning procedure depends upon the type of sample. After removing the bulk of the extracted sample matrix from the extraction vessel, the cell and end-frits should be scrubbed with an aqueous detergent, water and a stiff brush. Placing the parts in an ultrasonic bath with a warm detergent solution is very helpful. The parts should be rinsed with reagent water. The ultrasonic bath treatment should then be repeated with either methyl alcohol or acetone or both followed by air drying.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific Quality Control procedures and to Method 3500 for sample preparation quality control procedures.

8.2 Each time samples are extracted, and when there is a change in reagents, a reagent blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic

laboratory contamination. Any reagent blanks, matrix spike samples, or replicate samples should be subjected to exactly the same analytical procedures (Sec. 7.4) as those used on actual samples.

8.3 All instrument operation conditions and parameters should be recorded.

9.0 METHOD PERFORMANCE

9.1 Using Method 8310, an HPLC method with either UV/Vis or fluorescence detection, expected minimum detection limits are between 0.010 - 1.00 mg/kg depending upon the actual analyte and detector. The estimated quantitation limits (EQLs) would range from 0.10 - 10 mg/kg depending on analyte and detector. Using Method 8270, a GC/MS method, expected minimum detection limits are approximately 0.70 mg/kg. The estimated quantitation limits (EQLs) for GC/MS would be approximately 7 mg/kg. The MDLs and EQLs listed above are based on a 3-g sample.

9.2 Single laboratory precision and accuracy data based on this method (using a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two reference materials (one a lake sediment from Environment Canada and the other a marine sediment from the National Science and Engineering Research Council of Canada, both naturally contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. The data were taken from Reference 2. Average recoveries from six replicate extractions ranged from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions ranged from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in a table in Method 8270.

9.3 Single laboratory precision and accuracy data based on the use of a fixed restrictor and liquid trapping were obtained for twelve of the method analytes by the extraction of a certified reference material obtained from Fisher Scientific (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions ranged from 60 to 122% (overall average of 89%) based on the certified value. Following are the instrument conditions that were utilized to extract a 3.4 g sample: Pressure - 300 atm; Time - 60 min.; Extraction fluid - CO_2; Modifier - 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature - 80°C; Restrictor temperature - 120°C; and, Trapping fluid - chloroform (methylene chloride has also been used). The data are found in a table in Method 8270.

9.4 Single laboratory precision and accuracy data based on this method (using a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of a well-characterized reference material naturally contaminated with PAHs. The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by HPLC. Average recoveries from three replicate extractions ranged from 85.7 to 153% (overall average of 107%) based on the Soxhlet value. The data may be incorporated in a future revision of Method 8310.

10.0 REFERENCES

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11.0 SAFETY

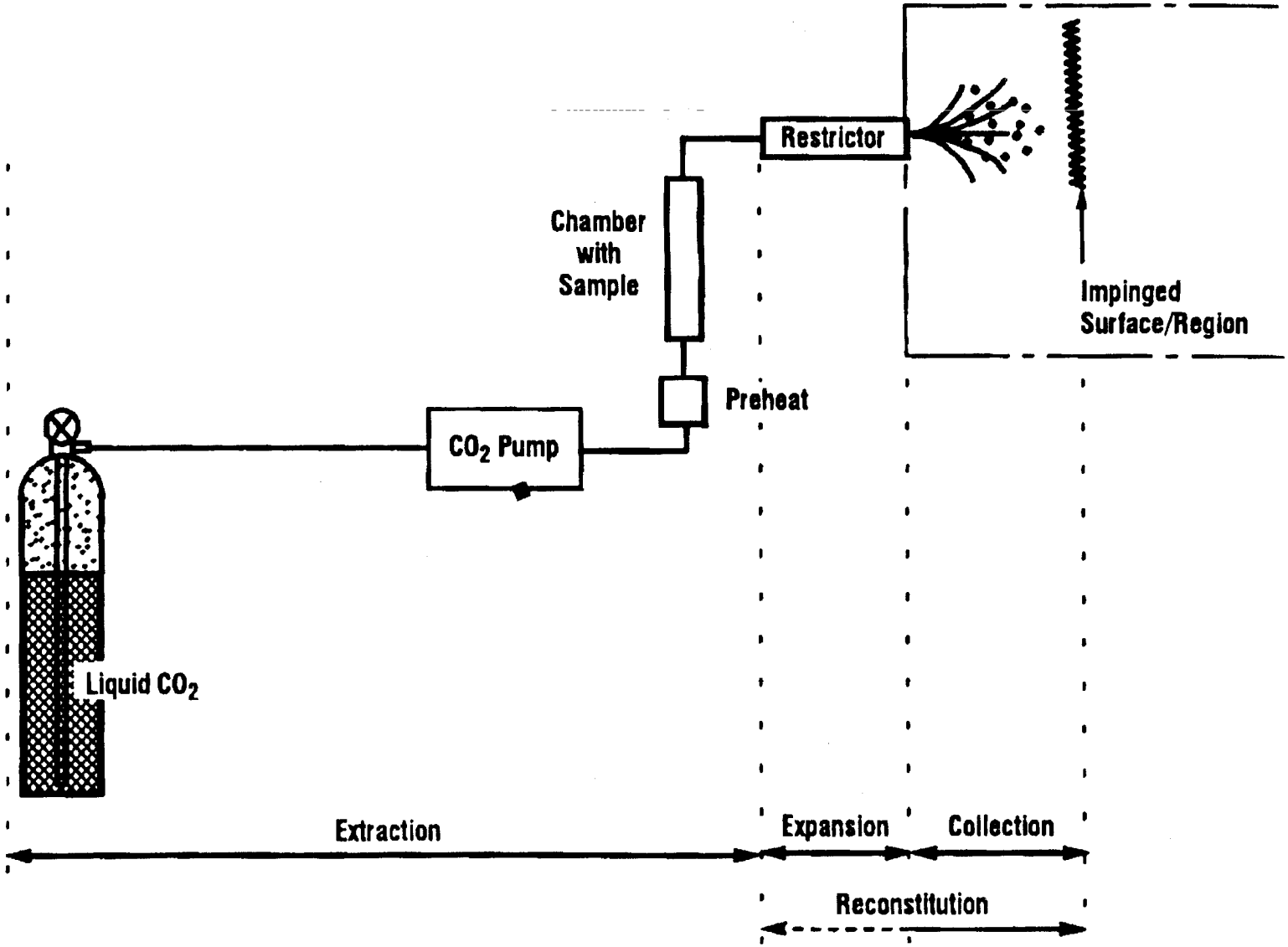
11.1 When liquid carbon dioxide comes in contact with skin, it can cause "burns" because of its low temperature (-78°C). Burns are especially severe when CO_2 is modified with organic liquids.

11.2 The extraction fluid, which may contain a modifier, usually exhausts through an exhaust gas and liquid waste port on the rear of the panel of the extractor. This port must be connected to a chemical fume hood to prevent contamination of the laboratory atmosphere.

11.3 Combining modifiers with supercritical fluids requires an understanding and evaluation of the potential chemical interaction between the modifier and the supercritical fluid, and between the supercritical fluid or modifier and the analyte(s) or matrix.

11.4 When carbon dioxide is used for cryogenic cooling, typical coolant consumption is 5 L/min, which results in a carbon dioxide level of 900 ppm for a room of 4.5 m x 3.0 m x 2.5 m, assuming 10 air exchanges per hour.

FIGURE 1
SCHEMATIC OF A TYPICAL SUPERCRITICAL FLUID EXTRACTION SYSTEM



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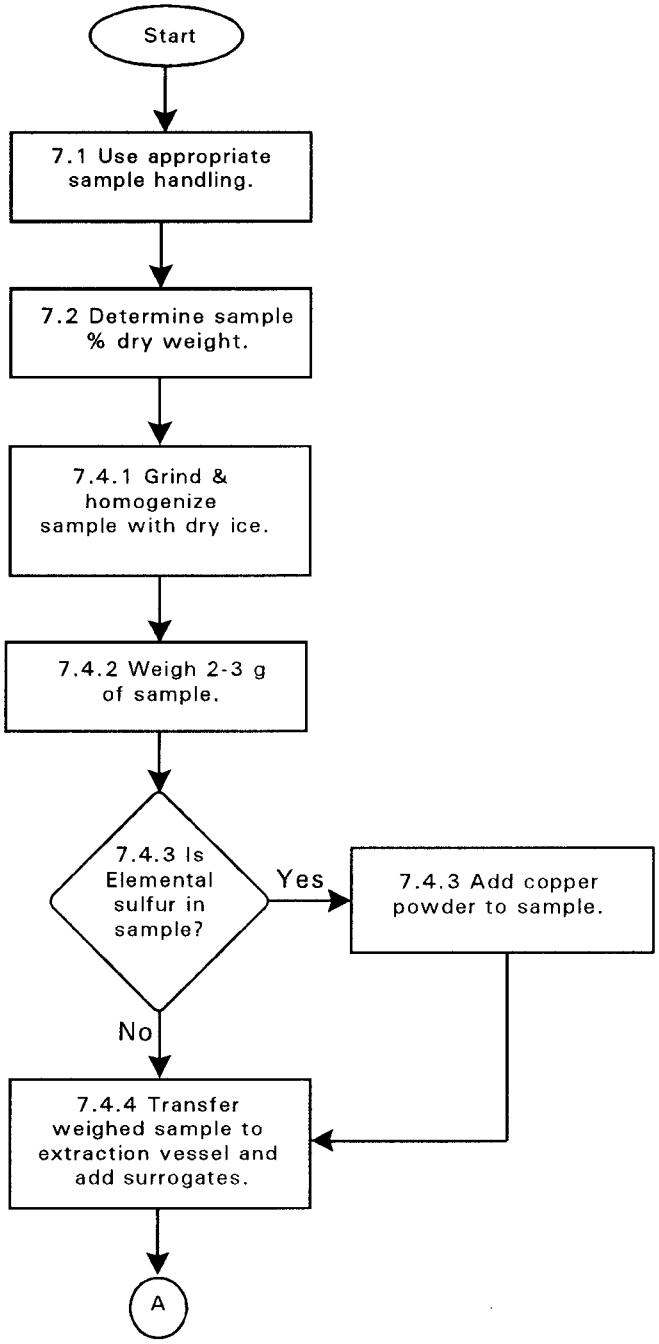

SUPERCRITICAL FLUID EXTRACTION OF POLYNUCLEAR AROMATIC HYDROCARBONS