METHOD 3560

SUPERCRITICAL FLUID EXTRACTION OF TOTAL RECOVERABLE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 3560 describes the use of supercritical fluids for the extraction of total recoverable petroleum hydrocarbons (TRPHs) 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 separation of the TRPHs from the matrices of concern.

1.2 Method 3560 is not suitable for the extraction of low-boiling TRPHs such as gasoline.

1.3 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 A known amount of sample is transferred to the extraction vessel. The sample is then extracted in the dynamic mode for up to 30 min with supercritical carbon dioxide at 340 atm, 80°C and a gas flow rate of 500 - 1000 mL/min.

2.2 After depressurization of the carbon dioxide, the extracted TRPHs are collected in a small volume of tetrachloroethene, methylene, isooctane, or other solvent appropriate for the determinative method (see Sec. 5.4), or on a sorbent material, depending on the SFE system used. In the latter case, the analytes are collected by rinsing the sorbent material with a solvent appropriate for the determinative method.

2.3 After collection, the TRPHs are analyzed by the appropriate determinative method.

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 (e.g., Methods 8015 or 8440). If glass wool and a drying agent are used with the sample, these materials should be included when performing a reagent blank check.

3.2 The extraction vessel(s), the frits, the restrictor(s), and the multi-port valve may retain solutes whenever high-concentration samples are extracted. It is, therefore, good practice to clean the extraction system after each extraction. Replacement of the restrictor may be necessary 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 (concentration in the high ppm range). If reagent blanks continue to indicate contamination, even after replacement of the extraction vessel and the restrictor, the multi-port valve must be cleaned.

4.0 APPARATUS AND MATERIALS

4.1 Supercritical fluid extractor and associated hardware.

WARNING: A safety feature to prevent overpressurization 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.

4.1.2 Extraction vessel - Stainless-steel vessel with end fittings and 0.5-or 2-µm frits. Use the extraction vessel supplied by the manufacturer of the SFE system being used. The PEEK (polyether ether ketone) extraction vessels supplied by Isco, Inc. are acceptable for use with the Isco SFE system.

Fittings used for the extraction vessel must be capable of withstanding the required extraction pressures. The maximum operating pressure for most extractors is 500 atm. However, extractors with higher pressure ratings are available. Check with the manufacturer of the particular extraction system on the maximum operating pressure and temperature for that system. Make sure that the extraction vessels are rated for such pressures and temperatures.

4.1.3 Restrictor - 50 µm ID x 150 or 375 µm OD x 25 to 60 cm length piece of uncoated fused-silica tubing (J&W Scientific or equivalent). Other restrictors may be used, including tapered restrictors, static pinhole restrictors, frit restrictors, or variable orifice restrictors (either manual or computer-controlled), crimped metal tubing, or polyether ether ketone (PEEK) tubing. Check with the manufacturer of the SFE system on the advantages and disadvantages of the various restrictor designs.

4.1.4 Collection device - The extracted TRPHs can be collected either in vials containing solvent, or they can be trapped on a sorbent material (e.g., octadecyl-bonded silica, stainless steel beads).

4.1.4.1 When the analytes are collected in solvent, install the restrictor through a hole made through the cap and septum of the vial, and position the restrictor end about 0.5 inch from the bottom of the vial. A syringe needle should also be inserted through the septum of the vial (with the tip positioned just below the septum) to prevent buildup of pressure in the vial. Use the type of vials appropriate for the SFE system used.

4.1.4.2 When the analytes are trapped on a sorbent material, it is important to ensure that breakthrough of the analytes from the trap does not occur. Desorption from the trapping medium can be accomplished by increasing the temperature of the trap and using a solvent to remove the analytes. Use the conditions suggested by the manufacturer of the particular system to recover the analytes.

4.2 Carbon dioxide cylinder balance (optional) - Balances from White Associates, Catalog No. 30, 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. The monitoring of carbon dioxide usage is optional and, if performed, may be accomplished by a variety of other means.

4.3 Tools required include: screwdriver (flat-blade), adjustable wrench, pliers, tubing cutter, and various small open-end wrenches for small fittings.

4.4 Magnesium sulfate monohydrate - may be used as received.

4.5 Silanized glass wool - requires high-temperature treatment (bake in a muffle furnace at 400°C for 2 to 4 hours) prior to use to remove any petroleum hydrocarbons.

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 than 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 (< 50 ppm water content), and it must be supplied in tanks with a full-length eductor tube.

5.3 Tetrachloroethene, C_2Cl_4 (spectrophotometric grade) - Used for the collection of TRPHs for determination by IR. Analyze a reagent blank to ensure no interferences are present at the TRPH wavelengths. Chlorofluorocarbons are not suitable for use with this method because of risk to the ozone layer.

5.4 Other pesticide-quality solvents may be used for the collection of TRPHs when these analytes are not determined by IR. The choice of solvent should be based on the determinative technique to be employed. For GC methods, methylene chloride or isooctane may be appropriate solvents. Because of concerns about stratospheric ozone depletion, chlorofluorocarbons (CFCs) are not appropriate solvents.

5.5 Copper filings - Copper filings added to remove elemental sulfur must have a shiny bright appearance to be effective. To remove oxides, treat with dilute nitric acid, rinse with reagent water to remove all traces of acid, rinse with acetone (copper will darken if acid is still present), and dry under a stream of nitrogen.

5.6 Drying agents - Anhydrous magnesium sulfate or diatomaceous earth.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Solid samples should be collected and stored as any other solid samples containing semivolatile organics.

6.2 See Chapter Four for guidance relating to semivolatile organics (including holding times).

7.0 PROCEDURE

7.1 Determination of sample % dry weight - In certain cases, sample results are desired based on a 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.

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

Immediately after weighing the sample for extraction, weigh an additional 5 - 10 g of the remaining sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

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

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

7.3 Sample handling

7.3.1 Decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves and rocks.

7.3.2 Weigh 3 g of sample into a precleaned aluminum dish. A drying agent (e.g., anhydrous magnesium sulfate or diatomaceous earth) may be added to samples that contain water in excess of 20% to increase porosity or to bind water. Alternatively, magnesium sulfate monohydrate is an excellent drying agent, and the amount of heat released (compared to anhydrous magnesium sulfate) is small, thereby minimizing the loss of volatile petroleum hydrocarbons. The amount of the drying agent will depend on the water content of the sample. Typically, a ratio of 1:1 works well for wet soils and sediment materials. However, a certain amount of water (up to 20 percent) in the sample has been shown to improve recoveries from certain matrices; therefore, if the sample is dry, water may optionally be added to bring the moisture content to approximately 20 percent.

7.3.2.1 If drying agent has been added to the sample, store the mixture of sample and drying agent for several hours (preferably overnight) at 4°C, with a minimum of headspace. This additional storage time is necessary to achieve acceptable analyte recovery. This step is not necessary if the alternate conditions described in Sec. 7.4.2.1 are used.

7.3.3 Transfer the weighed sample to a clean extraction vessel. The volume of the extraction vessel should match the sample volume. Use two plugs of silanized glass wool to hold the sample in place and fill the void volume (alternatively, drying agent or clean sand can be used to fill the void volume). Attach the end fittings, and install the extraction vessel in the oven. Always use clean frits for each extraction vessel.

7.4 Sample extraction

7.4.1 Fill the collection vessel with 3 mL of tetrachloroethene or other appropriate collection solvent. Chlorofluorocarbons are not suitable for use with this method because of risk to the ozone layer.

7.4.2 Set the pressure at 340 atm and the temperature at 80°C. Follow the manufacturer's instructions in setting up the instrument. Extract for 30 minutes in the dynamic mode. Note the safety precautions in Sec. 11.0 on venting the instrument into a chemical fume hood.

7.4.2.1 Alternatively, extract with a pressure greater than or equal to 340 atm at 150°C for 25 minutes, and a gas flow rate of 3500 to 4000 mL/min. These parameters dry the sample during the extraction, thus extended drying is not necessary for wet samples (Sec. 7.3.2.1).

7.4.2.2 A sorbent trap maintained above 0°C may be necessary for effective analyte trapping. The restrictor should resist plugging by water, since water released from the sample may pass through the restrictor.

7.4.3 After the extraction time has elapsed, the system should automatically switch to the equilibrate mode. At this point, remove the collection vessel(s) containing the extract. Since the depressurization of the carbon dioxide at the end of the restrictor outlet results in a gas flowrate of about 500 to 1000 mL/min, part of the collection solvent will evaporate during the extraction. However, cooling caused by the rapid expansion of the carbon dioxide limits the loss of solvent, so that approximately 2 mL remains (when tetrachloroethene is used) after a 30 min extraction. To prevent the collection solvent from freezing, place the collection vial in a beaker with warm water (approximately 25°C). The extract is then brought to the desired volume, or concentrated further. See Method 3510 for concentration techniques by micro Kuderna-Danish or nitrogen blowdown. Concentration must be performed in a chemical fume hood to prevent contamination of the laboratory environment.

7.4.4 The extract is ready for analysis by Method 8015, Nonhalogenated Volatile Organics by Gas Chromatography, or Method 8440, Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry.

7.5 SFE System Maintenance

7.5.1 Depressurize the system following the manufacturer's instructions.

7.5.2 After extraction of an especially tarry sample, the frits may require replacement to ensure adequate extraction fluid flow through the restrictor. In addition, very fine particles contained in samples can clog the frits necessitating replacement.

7.5.3 Clean the extraction vessel after each sample. The cleaning procedure depends on the type of sample. After removing the bulk of the extracted sample from the extraction vessel, the cell should be scrubbed with an ionic detergent, water, and a bottle brush. After extraction of tarry materials, use solvent rinses or an ultrasonic bath to clean the extraction vessel.

7.5.4 For samples known to contain elemental sulfur, use copper filings to remove the dissolved sulfur from the fluid. The copper filings (1 to 2 g per sample) can be packed in a separate extraction vessel connected to the outlet end of the sample extraction vessel, or they can be mixed with the sample, and a plug of copper filings can be loaded in the extraction vessel with the sample such that any sulfur extracted by the carbon dioxide can be removed before the stream of carbon dioxide containing the analytes reaches the restrictor.

7.5.5 The procedure to be followed in emptying the syringe pump depends upon the type of fluid being used. In the case of carbon dioxide, which is a gas at ambient temperature and pressure, it is only necessary to vent the gas to a fume hood by allowing it to expand across the purge valve. Follow the manufacturer's instructions in emptying the syringe pump.

7.5.6 To change fluid supply cylinders on a system with a syringe pump, it is necessary to empty the syringe pump as described in Sec. 7.5.5. Upon completion of the emptying procedure, the piston will be at its maximum extension, and the syringe pump outlet valve and purge valve will be open. Then proceed as follows:

7.5.6.1 Connect the new fluid supply cylinder to the syringe pump inlet line, and open the supply cylinder valve.

7.5.6.2 Open the pump inlet valve. The new fluid will flow through the inlet line to the syringe pump and out through the vent.

7.5.6.3 Close the syringe pump outlet valve and the vent/purge valve.

7.5.7 Restrictor removal and installation - Follow manufacturer's instructions. When using fused-silica restrictors, it may be necessary to replace the restrictor after each sample, especially when extracting samples contaminated with heavy oils.

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 operating conditions and parameters must be recorded.

9.0 METHOD PERFORMANCE

9.1 Refer to Methods 8440 and 8015 for performance data.

9.2 Use standard reference materials to establish the performance of the method with contaminated samples.

10.0 REFERENCES

1. Lopez-Avila, V., N.S. Dodhiwala, J. Benedicto, and R. Young, (W. Beckert, Project Officer), "SFE/IR for the Determination of Petroleum Hydrocarbons in Soils and Sediments", EPA 600/X-92-046, US EPA, Environmental Monitoring Systems Laboratory, Las Vegas, NV, April, 1992.

2. Pyle, S.M., and M.M. Setty, "Supercritical Fluid Extraction of High-Sulfur Soils with Use of a Copper Scavenger", Talanta, 1991, 38 (10), 1125-1128.

3. Bruce, M.L., "Supercritical Fluid Extraction (SFE) of Total Petroleum Hydrocarbons (TPHs) with Analysis by Infrared Spectroscopy", Proceedings of the Eighth Annual Waste Testing and Quality Assurance Symposium, July, 1992.

4. Messer, D.C. and Taylor, L.T., J.. Chromatog. Soc., 33, 290-296 (1995)

5. Tang, P.H., Ho, J.S., and Eichelberger, J.W., JAOAC Int., 74, 73-82 (1993)

6. Ezzell, J. and Richter, B.E., J. Microcolumn Separations, 4, 319-323 (1992)

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. The NIOSH time-weighted average (TWA) concentration is 9000 ppm (American Conference of Governmental Industrial Hygienists, 1991-1992).

METHOD 3560

SUPERCRITICAL FLUID EXTRACTION OF TOTAL RECOVERABLE PETROLEUM HYDROCARBONS