SEMIVOLATILE ORGANIC COMPOUNDS (PAHs AND PCBs) IN SOILS/SLUDGES AND SOLID WASTES USING THERMAL EXTRACTION/GAS CHROMATOGRAPHY/MASS SPECTROMETRY (TE/GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8275 is a thermal extraction capillary GC/MS procedure for the rapid quantitative determination of targeted PCBs and PAHs in soils, sludges and solid wastes. The following analytes can 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[a]pyrene	50-32-8
Benzo[b]fluoranthene	205-99-2
Benzo[g,h,i]perylene	191-24-2
Benzo[k]fluoranthene	207-08-9
4-Bromophenyl phenyl ether	101-55-3
1-Chloronaphthalene	90-13-1
Chrysene	218-01-9
Dibenzofuran	132-64-9
Dibenz[a,h]anthracene	53-70-3
Dibenzothiophene	132-65-0
Fluoranthene	206-44-0
Fluorene	86-73-7
Hexachlorobenzene	118-74-1
Indeno(1,2,3-cd)pyrene	193-39-5
Naphthalene	91-20-3
Phenanthrene	85-01-8
Pyrene	129-00-0
1,2,4-Trichlorobenzene	120-82-1
2-Chlorobiphenyl	2051-60-7
3,3'-Dichlorobiphenyl	2050-67-1
2,2',5-Trichlorobiphenyl	37680-65-2
2,3',5-Trichlorobiphenyl	3844-81-4
2,4',5-Trichlorobiphenyl	16606-02-3
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3
2,2',4,5'-Tetrachlorobiphenyl	41464-40-8
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2
2,3',4,4',5-Pentachlorobiphenyl	31508-00-6
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2

Compound	CAS No.[a]
2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0
2,2',3,3',4,4'-Hexachlorobiphenyl	38380-07-3
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	35694-08-7
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	2051-24-3

[a] Chemical Abstract Service Registry Number.

1.2 The estimated quantitation limit (EQL) of Method 8275 for individual PAH compounds is 1.0 mg/kg (dry weight) (0.2 mg/kg for individual PCB congeners) for soil/sediment samples and 75 mg/kg for wet sludges/other solid wastes (depending on water and solvent content). However, this can be lowered by adjusting the range of the calibration curve or introducing larger sample sizes if sample interferences are not a factor. Detection limits achievable during method development ranged from 0.01 to 0.5 mg/kg for compounds in the target analyte list in Sec. 1.1 (dry samples).

1.3 This method is restricted to use by or under the supervision of analysts experienced in the operation of a gas chromatograph and mass spectrometer and skilled in the interpretation of mass spectral data. Each analyst must demonstrate the ability to maintain control and generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A portion of sample (0.003-0.250 g, depending on the expected concentration) is weighed into a sample crucible.

2.2 The crucible is placed in a thermal extraction chamber and then heated to 340°C where it is held for 3 minutes.

2.3 Thermally-extracted compounds are swept into a GC equipped with a split/splitless injection port (split ratio set at ~35:1 for a low concentration sample or ~400:1 for a high concentration sample) and then concentrated on the head of GC column. Thermal desorption lasts 13 minutes.

2.4 The temperature program of the GC oven is adjusted to the specific temperature conditions required to elute the target analytes. The target analytes are swept into a mass spectrometer for qualitative and quantitative determination.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, calibration standards and internal standards must be evaluated for interferences.

3.2 Whenever a heavily concentrated sample is encountered the GC column can become over loaded and an ON-LINE bakeout (Sec. 7.2.1) followed by a method blank is necessary.

3.3 A maintenance bakeout (Sec. 7.5) is performed whenever the ON-LINE bakeout and subsequent blank analyses do not eliminate system contamination.

4.0 APPARATUS AND MATERIALS

4.1 Thermal extraction/gas chromatograph/mass spectrometer (TE/GC/MS) system

4.1.1 Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria of Method 8270.

4.1.2 Data system - A computer interfaced to the mass spectrometer should allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search the GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as a reconstructed ion chromatogram (RIC). Software must also be available that allows integrating the abundances of the RIC between specified time or scan-number limits.

4.1.3 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points in the concentration range of interest may be used.

4.1.4 Gas chromatograph - Must be equipped with a heated split/splitless capillary injection port, column oven, cryogenic cooling (optional). The oven temperature should be controllable from ambient to 450°C, and have programmable oven heating controls capable of rates of 1°C/min to 70°C/min.

4.1.5 Recommended capillary column - A fused silica coated with (5% phenyl)-methylpolysiloxane phase; 25-50 meter length x (0.25 to 0.32 mm) I.D. with 0.1 to 1.0 micron film thickness (OV-5 or equivalent), depending on analyte volatility and separation requirements.

4.1.6 Thermal extraction unit - The TE unit should be constructed such that the sample and any compounds extracted are permitted to contact only heated fused quartz surfaces during the extraction and transfer to the GC injection port. It is also imperative that all zones in the sample transfer path be kept at a minimum of 315°C. The unit must also have a bakeout capability of at least 650°C in the thermal extraction chamber and 450°C in the interface zone. It should also be noted that all components, crucibles, spatulas and tools that come in contact with the sample be constructed of fused quartz to permit total oxidation of any residues.

4.2 Fused quartz sample spatula.

4.3 Muffle furnace tray - for holding the crucibles while cleaning.

4.4 Stainless steel forceps for sample crucible handling.

4.5 Petri dishes - for sample crucibles; one for clean storage and one for dirty storage.

4.6 Sample staging disk.

4.7 Porous fused quartz sample crucibles.

4.8 Porous fused quartz sample crucible lids.

4.9 Muffle furnace - for cleaning sample crucibles, capable of heating to 800°C.

4.10 Cooling rack/pad - high temperature, ceramic or quartz.

4.11 Analytical balance - minimum 2 gram capacity, 0.01 mg sensitivity.

4.12 Mortar and pestle.

4.13 100- and 60-mesh sieves.

4.14 Sample vials - glass, with polytetrafluoroethylene (PTFE)-lined caps.

5.0 REAGENTS

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

5.2 Stock standard solutions (1000 mg/L) - Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality methylene chloride or other suitable solvent (some PAHs may require initial dissolution in small volumes of toluene or carbon disulfide) and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into bottles with PTFE-lined screw-caps. Store at -10°C to -20°C or less and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after 1 year or sooner if comparison with a quality control reference standard indicates a problem.

5.3 Intermediate standard solutions - An intermediate standard solution should be prepared containing all the target analytes for the calibration standard solutions (separate solutions for PAHs and PCBs) or all the internal standards for the internal standard solution. The recommended concentration is 100 mg/L.

5.4 GC/MS tuning standard - A methylene chloride solution containing 50 mg/L of decafluorotriphenylphosphine (DFTPP) should be prepared. Store at -10°C to -20°C or less when not being used.

5.5 Matrix spike standard - Prepare a spiking solution in methanol that contains five or more of the target compounds at 100 mg/L for solid samples. The selection of compounds should represent the boiling point range of the target compounds. The stock and intermediate standards may be prepared as in Secs. 5.2 and 5.3 or commercially prepared certified standards are also acceptable. The standards must be prepared independently from the calibration stock standards.

5.6 Blank soil used for the preparation of the calibration standard soil and internal standard soil is prepared as outlined below.

5.6.1 Obtain a clean (free of target analytes and interferences) sedimentary soil. Dry and then grind it in a mortar and pestle. Sieve the ground material through a 100 mesh sieve. Several 50 mg aliquots should be extracted by TE/GC/MS (or other techniques) to determine if any compounds are present that could interfere with the compounds in Tables 1 and 2.

5.6.2 If no interferences are found, 300-500 grams of dried and sieved blank soil is tumbled for 2 days in a clean glass container with a PTFE-lined cap to ensure homogeneity before the analytes are spiked onto the soil.

5.7 Internal standard soil - The internal standard is prepared on a blank soil (Sec. 5.6). The internal standard soil should contain all compounds listed in Table 3 at a concentration of 50 mg/kg for each compound. Commercially-prepared soil standards may be used if they are certified by the manufacturer or by an independent source.

5.8 Calibration standard soil - The calibration standard is prepared on a blank soil (Sec. 5.6). The calibration standard soil must contain all target analytes to be reported, at a concentration of 35 mg/kg for the PAHs and 10 mg/kg for the PCBs. The PCBs are prepared at a lower concentration because expected concentrations in soil are expected to be lower. If preferred, both the PAHs and PCBs may be prepared at the same concentration. See Table 1 (PAH) and Table 2 (PCB) for the analytes that have been tested by this method. Commercially-prepared soil standards may be used if they are certified by the manufacturer or by an independent source.

5.9 Preparation of the internal standard and calibration standards on a blank soil.

5.9.1 The 50 mg/kg internal standard soil and both the PAH calibration standard (35 mg/kg) and PCB Calibration Standard (10 mg/kg) soils are all prepared by the same technique. The intermediate standard solutions (Sec. 5.3) or commercially-prepared certified solutions are used for dosing a weighed amount of blank soil (Sec. 5.6). Weigh 20.0 g of blank soil (as prepared in Sec. 5.6) into a 4-oz. glass container. Water is added (5% by weight) to aid in the mixing and dispersal of analytes to the more polar sites in the soil, as occurs in nature. For an intermediate standard containing 100 mg/L of each compound: add 10.0 mL to the wetted blank soil for the internal standard soil; add 7.0 mL for the PAH calibration standard soil; and 2 mL for the PCB calibration standard soil. Add additional methylene chloride so that the total solvent provides a slight solvent layer above the soil. This helps to distribute the standard compounds homogeneously throughout the soil.

5.9.2 The solvent and water are allowed to evaporate at room temperature until the soil appears dry (usually overnight). The soil containers are tightly capped with PTFE-lined caps

and placed on a tumbler that slowly rotates and mixes the contents. All soils are tumbled for at least five days to ensure homogeneity.

5.9.3 Internal standard soil and calibration standard soil should be stored in amber glass vials with PTFE seal caps at -10°C to -20°C or less and protected from exposure to light and moisture. The soil standards should be stable for up to 90 days under these storage conditions. Internal standard and calibration standard soils should be checked frequently against the calibration solutions for signs of degradation. The check is performed by adding an equivalent concentration of standard solution to the frit in the sample crucible lid just prior to transfer of the crucible and lid to the thermal extraction unit.

5.9.4 Internal standard and calibration standard soils must be replaced if the above check indicates degradation.

NOTE: The more volatile PAHs and PCBs in the soil calibration standards may exhibit higher concentrations than the calibration solutions. This results from the possibility of evaporation losses from the crucible frit lid of the more volatile analytes.

5.10 Methylene chloride, methanol, carbon disulfide, toluene, and other appropriate solvents-Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

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

7.0 PROCEDURE

7.1 Sample crucible preparation

WARNING: Do not touch the crucibles with your fingers. This can result in a serious burn during removal from the muffle furnace. Clean crucibles can be contaminated with oils from the fingers. Always handle the sample crucibles and lids with stainless steel tweezers.

7.1.1 Turn on the muffle furnace for cleaning crucibles and let it heat to 800°C for at least 30 minutes.

7.1.2 To clean the crucibles, load the sample crucibles and lids into the muffle furnace tray and place in the oven. Leave in the muffle furnace for 15 minutes then remove tray and place on cooling pad (at least 15-20 minutes) before transferring crucibles to the "clean" petri dish.

7.1.3 All sample crucibles and lids should be pre-cleaned and placed in a covered petri dish. Prepare a sufficient number of crucibles and lids to prepare a 5-point calibration curve and/or for the number of sample analyses planned.

7.2 Initial calibration of the TE/GC/MS system

7.2.1 Set the TE/GC/MS to the following recommended conditions and bake out the system.

ON-LINE bakeout procedure -This procedure should be performed before each set of calibration runs. If the autosampler is used, this should be incorporated into the autosampling sequence.

IMPORTANT: Sample crucible must be removed from the thermal extraction unit BEFORE bakeout procedure begins. It is not necessary to acquire MS data during a bakeout although GC/MS data should be taken during analysis of a method blank (following a bakeout) to monitor system contamination.

GC initial column temp. and hold time:	35°C for 4 minutes
GC column temperature program:	35 to 325°C at 20°C/min
GC final column temperature hold:	325°C for 10 minutes
GC cool time:	325°C to 35°C in 4 minutes
GC injection port temperature:	335°C; splitless mode for entire run
MS transfer line temperature:	290 - 300°C
GC Carrier gas:	Helium at 30 cm/sec
TE transfer line temperature:	310°C
TE interface oven temperature:	335°C
TE helium sweep gas flow rate:	40 mL/min
TE sample chamber heating profile:	Hold 60°C for 2 min; 60 - 650°C in 12 min; hold 650°C for 2 min; cool to 60°C.

7.2.2 Set the TE/GC/MS system to the following recommended conditions for calibration and sample analysis assuming a 30-m capillary column (see Sec. 4.1.5).

Mass range:	45 - 450 amu
MS scan time:	1.0 to 1.4 scan/sec
GC initial column temp. and hold time:	35°C for 12 minutes
GC column temperature program:	35 - 315°C at 8°C/min
GC final column temperature hold:	315°C for 2 min (or until benzo(g,h,i)perylene elutes.
GC column cool rate:	315°C to 35°C in 4 minutes
GC injector type:	Split/splitless capillary; 35:1 split ratio
GC injection port temperature:	325°C
GC injection port setting:	Splitless for 30 sec, then split mode for remainder of run
MS transfer line temperature:	290 - 300°C
MS source temperature:	According to manufacturer's specifications
MS solvent delay time:	15 minutes
MS data acquisition:	Off at 49 minutes
Calibration Standard Soil weight:	See Sec. 7.2.5.3 for initial calibration.
Carrier gas:	Helium at 30 cm/sec
TE transfer line temperature:	310°C
TE interface Oven temperature:	335°C

TE helium sweep gas flow rate:	40 mL/min
TE sample heating profile:	hold 60°C isothermal for 2 min; 60 - 340°C in 8 min; hold 340°C for 3 min; cool 340 - 60°C for 4 min.

NOTE: All calibration standards and samples must be analyzed under the same split ratio settings.

7.2.3 Method blank - A blank should follow the ON-LINE bakeout using the conditions listed in Sec. 7.4.2. Acquire the MS data and determine that the system is free of target analytes and interferences at the project required Method Detection Limit (MDL). Make appropriate corrections if contamination is observed (i.e., bake out, change GC column, change TE sample chamber and/or transfer line).

7.2.4 The GC/MS system must be hardware tuned to meet the DFTPP criteria in Method 8270. Add 350 ng (because of the 35:1 split) of DFTPP to the frit in the lid of the crucible and analyze following the conditions in Sec. 7.2.2.

7.2.5 Initial calibration curve - Calibration standards at a minimum of five different concentrations should be run during the initial calibration of the system and after any maintenance procedures which may affect system performance. This calibration procedure should also be performed if there is more than a 20% drift from the initial calibration curve and the calibration verification unless system maintenance corrects the problem. Adjust the injection port split ratio to 35:1 for the following calibration standard soil concentration. Any future modifications of the split ratio require the preparation of a new initial calibration curve at the new split ratio.

7.2.5.1 Using forceps, remove a sample crucible from the clean dish and place on the analytical balance. Tare or establish the weight to the nearest 0.1 mg and place on a clean surface.

7.2.5.2 Weigh 10 mg (±3%) of internal standard soil (Sec. 5.7) into the sample crucible using a fused quartz sample spatula. Place crucible back on the balance and determine weight. Record current weight and tare balance for the next step.

7.2.5.3 Weigh the calibration standard soil into the crucible (according to guidance below on PAHs and PCBs) and record weight. Place a lid on the crucible and load into the Thermal Extraction Unit or position in the autosampler. All analysis information and conditions should be recorded in a sample log.

NOTE: If commercially-prepared standards are used, the weights may vary slightly from what are presented below. This is acceptable as long as the calibration curve is within the linear range of the GC/MS system.

PAH Standard:

50 mg (±3%) of 35 mg/kg PAH calibration standard soil (Sec. 5.9).

Repeat the process with 40, 20, 10, and 5 mg (±3%) of 35 mg/kg PAH calibration standard soil + 10 mg of 50 mg/kg IS soil into separate crucibles.

This results in 50, 40, 20, 10, and 5 ng respectively on column of each target analyte in the calibration standard.

PCB Standard:

50 mg (±3%) of 10 mg/kg PCB calibration standard soil (Sec. 5.9).

Repeat the process with 40, 20, 10, and 5 mg (±3%) of 10 mg/kg PCB calibration standard soil + 10 mg of 50 mg/kg IS soil into separate crucibles.

This results in 10, 8, 4, 2, and 1 ng respectively on column of each target analyte in the calibration standard.

NOTE: The sensitivity of the GC/MS system may require adjustment of the above standard weights (calibration and internal) either up or down.

7.2.5.4 A split ratio of 300 or 400:1 is recommended for high concentration samples. A new calibration curve at the higher split ratio is required using a calibration standard soil containing an appropriate concentration of target analytes (approximately 10 times more concentrated to achieve a similar concentration on column).

7.2.6 Analysis - Upon method start, the sample is loaded into the fused quartz sample chamber. The sample chamber is heated to 340°C and held isothermal for 3 minutes. Helium carrier/sweep gas passes through the sample chamber at a flow rate of 40 mL/min. Thermally-extracted compounds are swept through a deactivated fused silica line into the GC injection port where they are split (low ~35:1) or (high ~400:1) before being concentrated on the head of the GC column which is held isothermal at 35°C. Once thermal extraction is complete (13 min.), the sample chamber is cooled, the GC oven is heated to 315°C at a rate of 10°C/min. (or according to required separation needs). Exact thermal extraction method parameters may be adjusted according to separation requirements.

7.2.7 Calculate response factors (RFs) for each analyte (using the internal standard assignments given in Tables 4 and 5) and evaluate the linearity of the calibration as described in Sec. 7.0 of Method 8000.

7.3 Calibration verification of the TE/GC/MS system

7.3.1 Prior to analysis of samples, the DFTPP tuning standard must be analyzed. Follow the guidance in Sec. 7.2.4. The DFTPP criteria must be demonstrated during each 12-hour shift.

7.3.2 At the beginning of each 12-hour shift, a method blank is analyzed using the conditions in Sec. 7.2.2. Also, the mg of calibration standard soil used for the midpoint of the initial calibration curve and 10 mg of internal standard soil are analyzed and the RF values are calculated for each target analyte. Calculate the % difference for each target analyte as described in Sec. 7.0 of Method 8000. If the RF values of each target analyte are not within 20% of their mean RF values determined during the initial calibration, then the initial calibration sequence must be repeated unless a calibration verification standard analyzed after system maintenance meets the % difference criteria.

7.3.3 After every 6 hours of operation, a method blank is analyzed to verify that the system is still clean.

7.4 Sample preparation, weighing and loading

7.4.1 Sample preparation - Decant and discard any water layer on a sediment sample. Discard any foreign objects such as pieces of wood, glass, leaves and rocks. Sample preparation requires homogenizing the wet or dry sample as well as possible and selecting a representative aliquot for analysis. Extremely wet samples (high H_2O and solvents) can cause excessive pressure in the MS if too much sample is inserted in the system. See Sections 7.4.3.1 and 7.4.3.2 as guidelines for sample weight and moisture considerations.

7.4.2 Determination of sample % dry weight - In certain cases involving soil/sediment samples, sample results are desired based on a dry-weight basis. When such data are desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination. Also, for any sample that appears to contain moisture, the % moisture must be calculated to determine whether drying of the sample is necessary prior to grinding in a mortar and pestle (see Secs. 7.4.3 and 7.4.4).

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

Weigh 5-10 g of a portion of 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. Discard this portion after weighing as a separate (unheated) portion will always be used for analysis. Calculate the % dry weight as follows:

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

$$\%\ \text{moisture} = 100 - (\%\ \text{dry weight})$$

7.4.3 Wet Samples (greater than 20% moisture)

7.4.3.1 For samples where naphthalenes are target analytes:

Perform the following steps quickly to minimize sample exposure to air, thereby causing possible loss of naphthalenes as well as sample weight variability because of loss of moisture. Tare the crucible, weigh 10 mg of IS soil, then add 10-20 mg of a wet, representative sample portion. Record the sample weight and insert the crucible into the TE Inlet system.

7.4.3.2 For wet samples where naphthalenes are not target analytes:

A representative aliquot (3-5 grams) of sample should be spread in a thin layer in a clean shallow container and air dried at room temperature (25°C) in a hood for 30 - 40 minutes.

7.4.3.2.1 Thick layers of clay type sediment may require longer drying periods.

NOTE: No heat should be used to aid drying.

7.4.3.2.2 When dry, scrape the sample loose from the container walls and break into uniform particle size or grind in a mortar and pestle until reasonably uniform and homogeneous in texture. Sieve through a 60-mesh sieve and store in a sample vial.

7.4.4 Dry samples (less than 20 % water)

To prepare dry samples, homogenize 5-10 grams in a mortar and pestle and sieve through a 60-mesh screen and store in a sample vial.

7.4.5 Internal standard weighing

7.4.5.1 Using forceps, remove a sample crucible from the clean dish and place on the analytical balance. Tare or establish the weight to the nearest 0.1 mg and place on a clean surface.

7.4.5.2 Weigh 10 mg (±3%) of internal standard soil mixture into the sample crucible using a fused quartz sample spatula. Place crucible back on the balance and determine weight. Record current weight and tare balance for the next step.

7.4.6 Sample weighing - An aliquot (3 - 250 mg) of the prepared sample is removed with a clean fused quartz spatula and placed in the sample crucible and its weight determined. The weight of the sample to be loaded into the thermal extraction crucible should be determined as follows:

7.4.6.1 If low levels (0.02 - 5.0 mg/kg and low total organic content) are expected, 100 to 250 mg of (dry) sample should be weighed (assuming a 35:1 split ratio).

NOTE: As per Sec. 1.2, the estimated quantitation limit of this method is 1 mg/kg. Any concentrations that are determined to be lower than 1 mg/kg would be considered estimated concentrations.

7.4.6.2 If high levels (500-1500 mg/kg and high total organic content) are expected, 3 to 5 mg of (dry) sample should be weighed (assuming a 35:1 split ratio).

7.4.6.3 For intermediate levels, adjust the weights accordingly.

7.4.6.4 If the expected concentration exceeds 1500 mg/kg, a greater split ratio is required. A split ratio of 300 to 400 is recommended. This, of course, requires an initial calibration curve developed with the selected split ratio.

7.4.6.5 For samples of unknown concentration or total organic content, weigh less than 20 mg of sample for the initial run.

NOTE: It is highly recommended that samples of unknown concentration be screened prior to TE/GC/MS analysis. This will prevent the need to reanalyze samples as well as protect the system from overload which causes downtime while performing system maintenance. The screening may be performed using the optional FID device that is available as an add-on to the TE/GC/MS device or by using a rapid

semiquantitative extraction with methylene chloride and injection on a GC/FID to determine relative concentrations.

7.4.6.6 Select a sample for matrix spike determination (see Method 3500 for guidance). Weigh one or two portions into crucibles containing internal standard (see same section cited above for guidance on whether to analyze a matrix spike duplicate or a duplicate sample). Add 5.0 µL of the matrix spike standard (Sec. 5.5) directly to the sample, immediately cover with lid and transfer to the thermal extraction unit or the autosampler.

7.4.7 Loading sample - Make sample concentration assessment and weigh sample into crucible containing the previously weighed internal standard soil. Record sample weight (to the nearest 0.1 mg), cover the crucible with lid and place covered crucible into the thermal extraction unit or autosampler tray. If the sample is wet and/or target compounds have a higher volatility than n-dodecane, the autosampler tray should be chilled to 10-15°C.

7.4.8 Analysis - The sample is loaded into the fused quartz sample chamber of the thermal extraction unit. See Sec. 7.2.7 for details on the operation of the TE/GC/MS system.

7.4.8.1 For extremely low concentration samples where the signal to noise ratio is less than 3:1, increase sample size as appropriate from detector response after repeating Sec. 7.4.5.

7.4.8.2 If too much sample is extracted and GC column overloading is evident, bake out system (as in Sec. 7.2.1) and analyze a blank to determine if additional system cleaning is necessary (Sec. 7.2.3). Use a smaller aliquot of the sample (decreasing sample size as required) after repeating Sec. 7.4.5.

7.5 Maintenance bakeout procedure

7.5.1 System bakeout conditions: For OFF-LINE (no autosampling) conditions following an extremely overloaded system and for routine cleaning maintenance.

IMPORTANT: Sample crucible must be removed from the thermal extraction unit BEFORE bakeout procedure begins.

Before this bakeout procedure, the TE interface oven should be cooled so that the fused silica transfer line capillary can be removed. Following the bakeout a new transfer line capillary should be installed.

GC initial column temp. and hold:	335°C, hold for 20 minutes
GC injection port temperature:	335°C; set in split mode
MS transfer line temperature:	295 - 305°C
GC Carrier gas:	Helium at 30 cm/sec
TE transfer line temperature:	OFF; until new capillary installed
TE interface oven temperature:	400°C
TE sweep gas flow rate:	MAX; approx 60 mL/min;
TE sample chamber heating profile:	Heat to 750°C and hold 700°C for 3 min; cool to 60°C.

7.6 Qualitative analysis

Follow the procedures in Method 8270, Sec. 7.0, to identify target compounds.

7.7 Quantitative analysis

Identified compounds are quantitated via the internal standard calibration technique using the integrated abundance from the EICP of the primary characteristic ion. The internal standard used should be assigned according to Table 4. Calculate the concentration of each identified analyte as follows:

$$C_x = \frac{(A_x)(C_{is})(W_{is})}{(\overline{RF})(A_{is})(W_x)(D)}$$

where:

C_x = Concentration of compound being measured (mg/kg).
A_x = Area of characteristic ion for compound being measured in sample.
C_{is} = Concentration of internal standard soil (mg/kg).
W_{is} = Weight of internal standard soil (kg).
W_x = Weight of sample (kg).
$\overline{RF}$ = Mean response factor for compound being measured from initial calibration curve.
A_{is} = Area of characteristic ion for the internal standard.
D = (100 - % moisture in sample)/100, or 1 for wet-weight basis.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. Required instrument QC is found in the following sections of Method 8275:

8.2.1 The GC/MS system must be tuned to meet the DFTPP specifications in Secs. 7.2.4 and 7.3.1.

8.2.2 There must be an initial calibration of the GC/MS system as specified in Sec. 7.2.

8.2.3 The GC/MS system must meet the calibration verification criteria specified in Sec. 7.3 each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this

demonstration. NIST (National Institute of Standards and Technology) Standard Reference Material (SRM) #1939 may be used to monitor method performance and document data quality. An SRM with PAHs may be substituted if PAHs are the primary target analytes.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Multilaboratory precision data for PAHs and for a few semivolatile compounds are presented in Table 5. The results are based on the analysis of test soils spiked at 10 mg/kg and analyzed by 3 different laboratories. A Ruska ThermEx inlet interfaced to a GC/MS system was utilized to develop the data. A total ion chromatogram generated by TE/GC/MS of PAH analysis is shown in Figure 1.

9.2 Multilaboratory performance data for PCB congeners are presented in Table 6. The results are based on analyses of NIST Standard Reference Material (SRM) #1939 using Method 8275A (Reference 1). A Ruska ThermEx inlet interfaced to a GC/MS system was utilized to develop the data. An ion chromatogram generated by TE/GC/MS of PCB congeners is shown in Figure 2.

10.0 REFERENCES

1. Worden, R., "Method 8275A: Quantitative Addendum For SW-846 Method 8275", Research report to the U.S. Environmental Protection Agency; Ruska Laboratories, Inc., Houston, TX, 1993.

2. Snelling, R., King, D., Belair, B., "Analysis of PAHs in Soils and Sludges Using Thermal Extraction-GC-MS", Application Note 228-228; Hewlett-Packard Co., Wilmington, DE, 1993.

3. King, D., Belair, B., "Analysis of PCBs in Soils and Sludges Using Thermal Extraction-GC-MS", Application Note 228-229; Hewlett-Packard Co., Wilmington, DE, 1993.

TABLE 1

PAH/SEMIVOLATILE CALIBRATION STANDARD SOIL AND QUANTITATION IONS

Compound	Quantitation Ion
1,2,4-Trichlorobenzene[1]	180
Naphthalene	128
Acenaphthylene	152
Acenaphthene	153
Dibenzofuran	168
Fluorene	166
4-Bromophenyl phenyl ether[1]	248
Hexachlorobenzene[1]	284
Phenanthrene	178
Anthracene	178
Fluoranthene	202
Pyrene	202
Benzo[a]anthracene	228
Chrysene	228
Benzo[b]fluoranthene	252
Benzo[k]fluoranthene	252
Benzo[a]pyrene	252
Indeno(1,2,3-cd)pyrene	276
Dibenz[a,h]anthracene	278
Benzo[g,h,i]perylene	276

[1] This analyte may be deleted if the target analytes are PAHs only.

All compounds are present at 35 mg/kg.

TABLE 2

PCB CALIBRATION STANDARD SOIL

IUPAC #	CAS #	Compound Name	Quantitation Ion
1	2051-60-7	2-Chlorobiphenyl	188
11	2050-67-1	3,3'-Dichlorobiphenyl	222
18	37680-65-2	2,2',5-Trichlorobiphenyl	258
26	3844-81-4	2,3',5-Trichlorobiphenyl	258
31	16606-02-3	2,4',5-Trichlorobiphenyl	258
52	35693-99-3	2,2',5,5'-Tetrachlorobiphenyl	292
49	41464-40-8	2,2',4,5'-Tetrachlorobiphenyl	292
44	41464-39-5	2,2',3,5'-Tetrachlorobiphenyl	292
66	32598-10-0	2,3',4,4'-Tetrachlorobiphenyl	292
101	37680-73-2	2,2',4,5,5'-Pentachlorobiphenyl	326
118	31508-00-6	2,3',4,4',5-Pentachlorobiphenyl	326
138	35065-28-2	2,2',3,4,4',5'-Hexachlorobiphenyl	360
187	52663-68-0	2,2',3,4',5,5',6-Heptachlorobiphenyl	394
128	38380-07-3	2,2',3,3',4,4'-Hexachlorobiphenyl	360
180	35065-29-3	2,2',3,4,4',5,5'-Heptachlorobiphenyl	394
170	35065-30-6	2,2',3,3',4,4',5-Heptachlorobiphenyl	394
194	35694-08-7	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	430
206	40186-72-9	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	392
209	2051-24-3	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	426

All compounds are present at 10.0 mg/kg

TABLE 3

INTERNAL STANDARD SOIL

Compound	Quantitation Ion
2-Fluorobiphenyl	172
Phenanthrene-d_{10} [1]	188
Benzo[g,h,i]perylene ($^{13}C_{12}$)	288

[1] This internal standard is more susceptible to soil microbial degradation. It is suggested that a ^{13}C-labeled phenanthrene be substituted.

TABLE 4

INTERNAL STANDARDS WITH CORRESPONDING PAH ANALYTES ASSIGNED FOR QUANTITATION

2-Fluorobiphenyl

Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
All PCB Congeners from Table 2

Phenanthrene-d10

Phenanthrene
Anthracene
Fluoranthene
Pyrene

Benzo(g,h,i)perylene($^{13}C_{12}$)

Benzo[a]anthracene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[a]pyrene
Indeno(1,2,3-cd)pyrene
Dibenz[a,h]anthracene
Benzo[g,h,i]perylene

TABLE 5

MULTI-LABORATORY PRECISION DATA FROM OF ANALYSIS OF SAMPLES CONTAINING PAHs/SEMIVOLATILES USING TE/GC/MS[a]

#	Compound	Quant. Ion	Results for 10 mg/kg	
			Mean	RSD (%)
1	1,2,4-Trichlorobenzene[b]	180	11.0	35.7
2	Naphthalene	128	13.0	45.3
3	Acenaphthylene	152	10.4	18.1
4	Acenaphthene	153	11.1	22.6
5	Dibenzofuran	168	10.8	22.9
6	Fluorene	166	11.0	24.0
7	4-Bromophenyl phenyl ether[b]	248	11.1	17.6
8	Hexachlorobenzene[b]	284	10.8	18.5
9	Phenanthrene	178	10.6	20.2
10	Anthracene	178	10.9	34.4
11	Fluoranthene	202	10.7	17.0
12	Pyrene	202	10.8	19.9
13	Benzo[a]anthracene	228	10.1	24.1
14	Chrysene	228	10.4	17.8
15	Benzo[b]fluoranthene	252	10.9	23.1
16	Benzo[k]fluoranthene	252	10.4	30.0
17	Benzo[a]pyrene	252	10.9	25.7
18	Indeno(1,2,3-cd)pyrene	276	11.0	21.5
19	Dibenz[a,h]anthracene	278	10.5	25.8
20	Benzo[g,h,i]perylene	276	10.8	21.5

[a] These data are the compiled results of studies done by three different laboratories. These results are from samples spiked at 10 mg/kg.

[b] Not a PAH.

Data are taken from Reference 1.

TABLE 6

MULTI-LABORATORY COMPARISON OF NIST ANALYSIS OF PCB SRM #1939 (River Sediment)
TO ANALYSIS OF PCB SRM BY TE/GC/MS

IUPAC No.	Compound	Quant. Ion	NIST[a] Conc. (mg/kg)	TE/GC/MS[b] Conc. (mg/kg)	% Recovery of NIST SRM	RSD (%)[b]
18	2,2',5-Trichlorobiphenyl	258	3.46	2.41	70	0.30
26	2,3',5-Trichlorobiphenyl	258	4.20	5.62	134	0.92
28+31[d]	2,4,4'- and 2,4',5-Trichlorobiphenyl	258	9.07[c]	12.09[b]	133	1.63
52	2,2',5,5'-Tetrachlorobiphenyl	292	4.48	4.67	104	0.57
49	2,2',4,5'-Tetrachlorobiphenyl	292	3.78	3.89	103	0.98
44	2,2',3,5'-Tetrachlorobiphenyl	292	1.07	0.95	89	0.16
66	2,3',4,4'-Tetrachlorobiphenyl	292	0.93	1.02	110	0.17
10	2,2',4,5,5'-Pentachlorobiphenyl	326	0.82	0.91	111	0.19
118	2,3',4,4',5-Pentachlorobiphenyl	326	0.51	0.70	137	0.14
138	2,2',3,4,4',5'-Hexachlorobiphenyl	360	0.57	0.58	102	0.12
187	2,2',3,4',5,5',6-Heptachlorobiphenyl	394	0.18	0.14	78	0.06
128	2,2',3,3',4,4'-Hexachlorobiphenyl	360	0.10	0.08	80	0.04
180	2,2',3,4,4',5,5'-Heptachloro-biphenyl	394	0.16	0.12	75	0.05
170	2,2',3,3',4,4',5-Heptachloro-biphenyl	394	0.11	0.06	55	0.05

[a] NIST mean concentration of 9 determinations from the analysis of SRM No. 1939 (PCBs in River Sediment A) by Soxhlet Extraction/single column GC/ECD.

[b] Mean concentration of 3 studies from the analysis of NIST SRM No. 1939 by TE/GC/MS; 21 soil analyses.

[c] PCB 28 and PCB 31 were unresolved. The value is the total of both compounds.

[d] The concentrations of PCB 28 and PCB 31 were added for comparison purposes.

Data are taken from Reference 1.

FIGURE 1

CHROMATOGRAM GENERATED BY TE/GC/MS OF PAH COMPOUNDS TYPICAL PAH CALIBRATION SOIL STANDARD

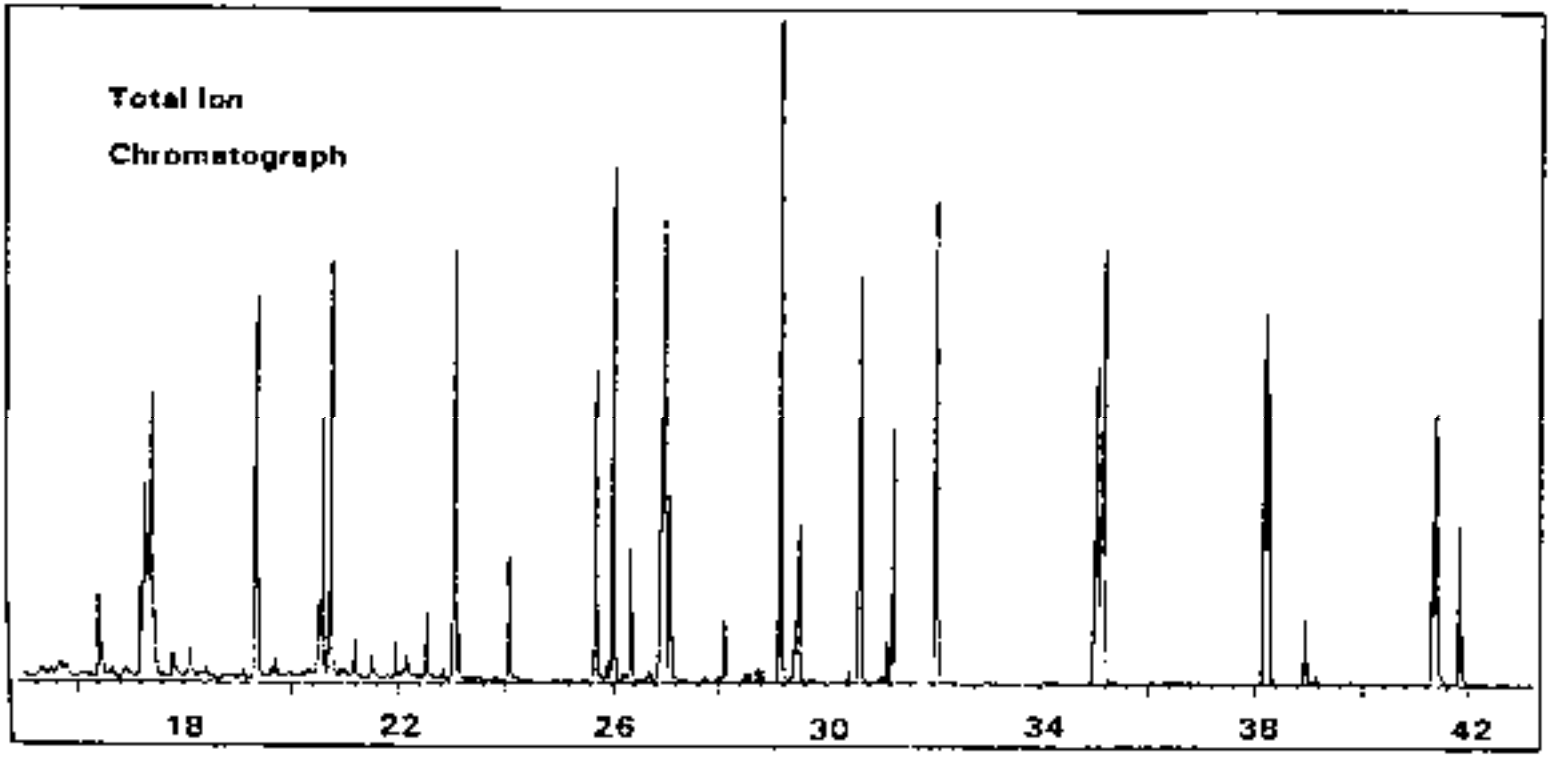
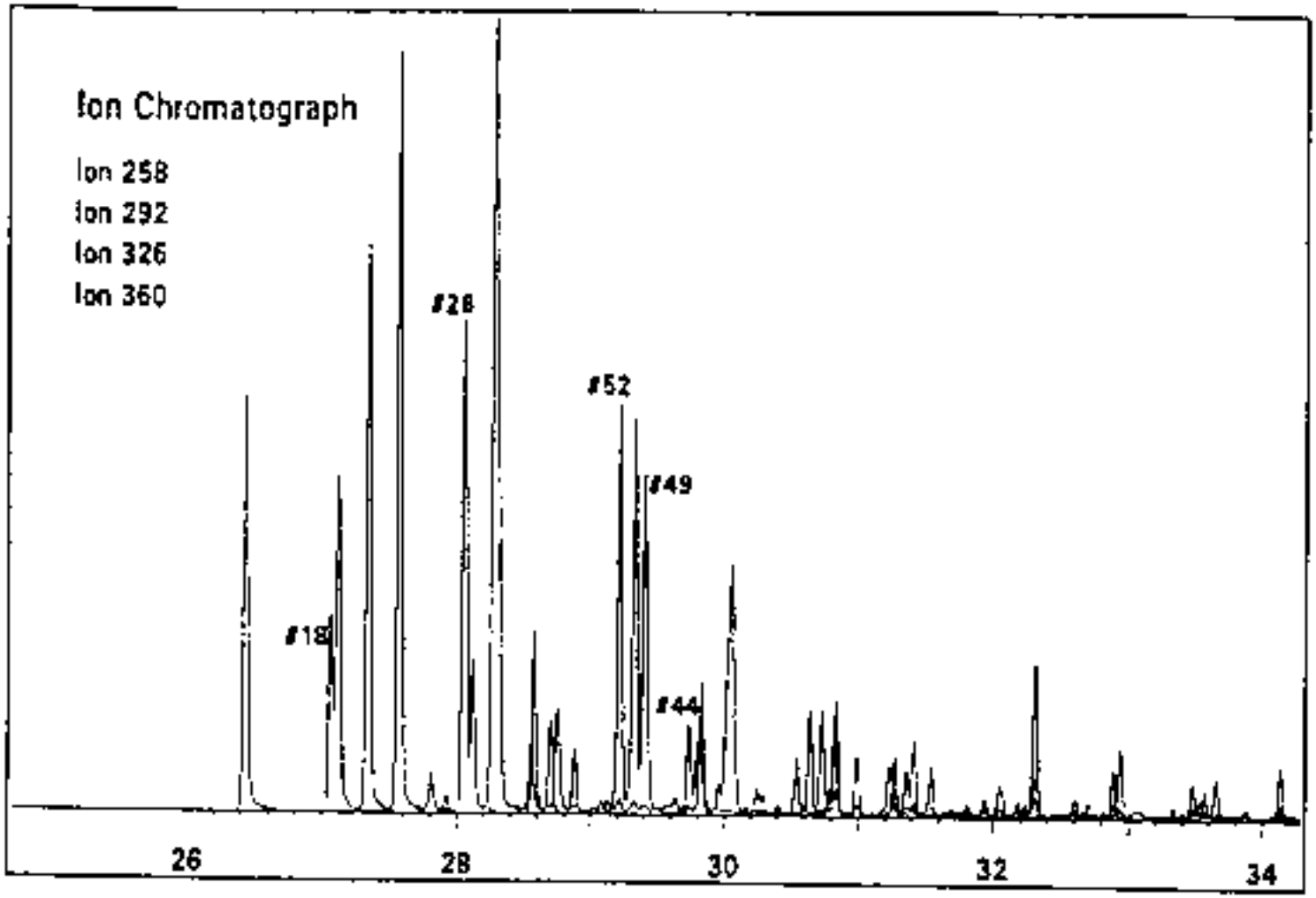
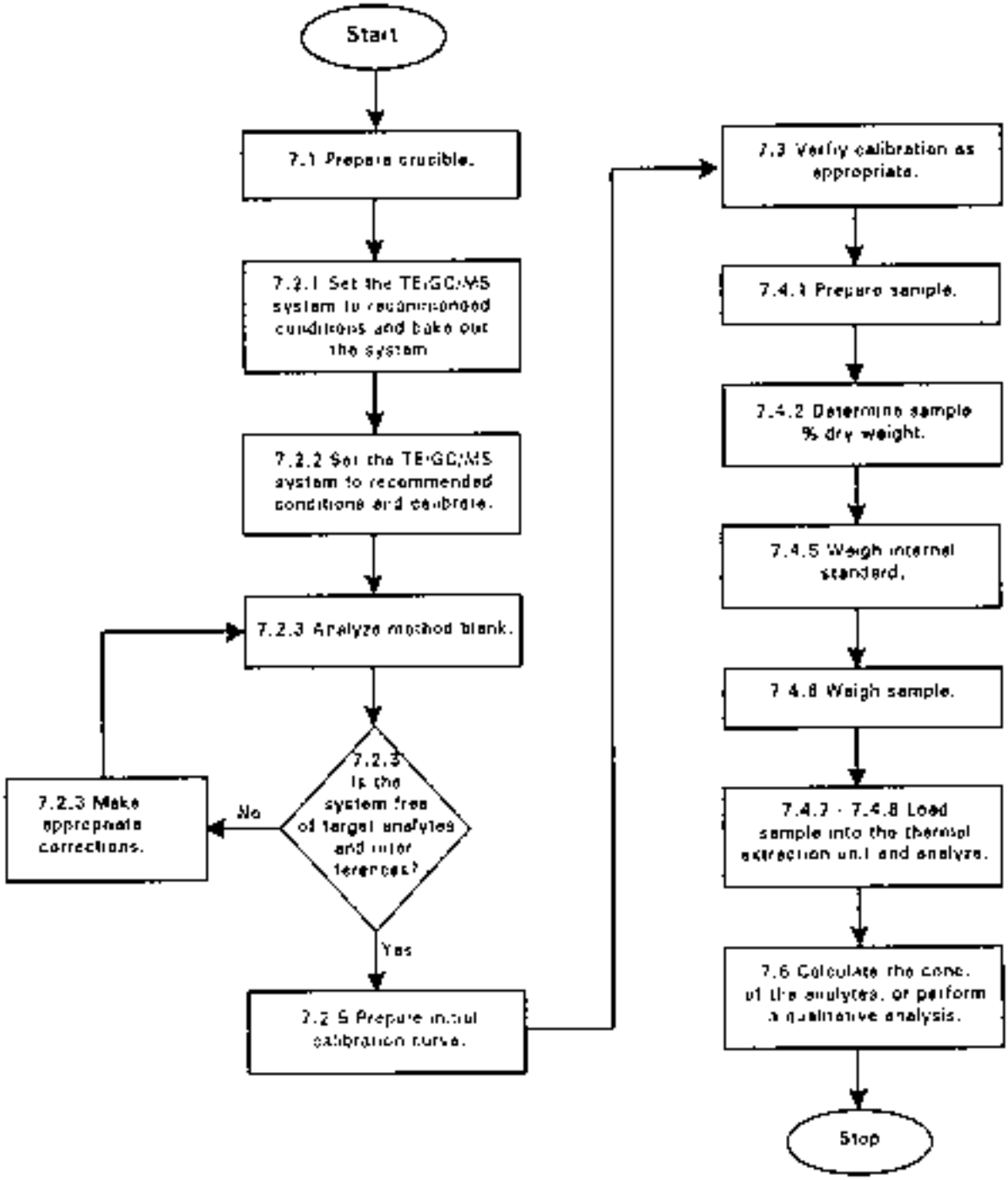


FIGURE 2

CHROMATOGRAM GENERATED BY TE/GC/MS OF PCB CONGENERS NIST SRM #1939 - PCBs IN RIVER SEDIMENT A




Start
7.1 Prepare crucible.
7.2.1 Set the TE/GC/MS system to recommended conditions and bake out the system
7.2.2 Set the TE/GC/MS system to recommended conditions and calibrate.
7.2.3 Analyze method blank.
7.2.4 Is the system free of target analytes and interferences?
No
7.2.3 Make appropriate corrections.
Yes
7.2.5 Prepare initial calibration curve.
7.3 Verify calibration as appropriate.
7.4.1 Prepare sample.
7.4.2 Determine sample % dry weight.
7.4.5 Weigh internal standard.
7.4.6 Weigh sample.
7.4.7 - 7.4.8 Load sample into the thermal extraction unit and analyze.
7.6 Calculate the conc. of the analytes, or perform a qualitative analysis.
Stop