USEPA Procedures for Wastewater Analyses by Packed Column GC and HPLC

This bulletin outlines the United States Environmental Protection Agency's procedures for analyzing 113 organic priority pollutants in wastewater. The chromatographic column or column packing listed by the EPA, and its Supelco equivalent, are described for each gas chromatographic-mass spectrometric, gas chromatographic, or high performance liquid chromatographic method. Confirmational columns and traps for concentrating analytes from samples are described for methods in which they are specified. The analyses are illustrated with chromatograms.

Key Words

- wastewater • priority pollutants • volatile pollutants
- acidic pollutants • base/neutral pollutants • pesticides
- PCBs

The United States Environmental Protection Agency (USEPA) has amended its priority pollutant protocol (1) by revising the gas chromatographic-mass spectrometric methods (GC-MS) and developing alternative gas or high performance liquid chromatographic methods (GC or HPLC) for organic water pollutant analyses. These alternative methods of analysis enable each regulated industry to choose the approach that suits its individual needs or capabilities. The EPA considers these methods, described in the *Federal Register* (2), to be the only validated analytical approach to monitoring priority pollutants in wastewater. Industries are required to use the methods both in evaluating their wastewater and in applying for National Pollution Discharge Elimination System (NPDES) permits (3). Deviations from these methods require EPA approval in advance. General information about the procedures follows, preceding illustrations and brief outlines of the analyses.

GC-MS Analyses for Organic Pollutants

For the revised GC-MS analyses, the organic pollutants are classified as volatiles or as nonvolatile acids (phenols), base-neutrals, and pesticides and PCBs, as they were in the 1977 protocol (1). The chromatographic columns described in the original protocol, however, have been replaced with columns developed through advanced column technology. The newer packings are more thoroughly deactivated than the packings they replace, and use of the columns listed in the revised methods improves the detection of priority pollutants. The GC-MS analyses for the organic compounds are incorporated into two methods, Method 624 for volatiles and Method 625 for nonvolatiles.

GC or LC Organic Pollutant Analyses

The GC or HPLC methods (Methods 601-613) simplify chromatographic analyses by separating 113 organic pollutants into 13 classes and describing an analysis for each class. Each GC or HPLC analysis specifies the use of a chromatographic column that will resolve all of the pollutants in one class and a detection system that is specific for their identification (2). Certain methods also suggest using a confirmational column to substantiate the identity of the pollutants.

Supelco GC packings were used by the EPA to evaluate these methods for priority pollutant analyses. Supelco packings are listed by the EPA in many of the methods, and for most of the other methods Supelco packings are generically equivalent alternatives to the listed packings. Supelco packings and columns were used to obtain all of the chromatograms in this bulletin.

Concentration of Organic Pollutants

Organic pollutants normally are present at ppb or lower levels in wastewater samples, and they must be concentrated prior to chromatographic analysis. The volatile organics are purged from the water sample and are trapped on solid adsorbents (GC-MS Method 624 or GC Method 601, 602, or 603). The recommended purge-trap method has been described by Bellar and Lichtenberg (4). After the organics are adsorbed, they are rapidly heat desorbed from the trap onto the chromatographic column. The EPA recommends a different adsorbent trap for each of the four methods of analysis for volatile pollutants. Each trap provides the best trapping efficiency for the volatile compounds listed in the corresponding method.

The nonvolatile organics are concentrated by solvent extraction of the water sample followed by concentration of the extract to 1 mL in a Kuderna-Danish concentrator. Subsequently, the extract is dried on a sodium sulfate column. When water samples are extremely dirty, specific cleanup procedures are used with each extraction method. Details of the extraction techniques and cleanup procedures are given in the *Federal Register* (2).

Outlines of EPA Methods

Outlines of the GC-MS methods for organic pollutant analyses are presented first, followed by outlines of the GC and HPLC methods. Each method outline lists the class of organic compounds, the concentration technique, the column, the confirmational column (if any), the detector, and any qualifications or potential problems that have been indicated by the EPA. For methods in which the listed packing is not a Supelco packing, the Supelco equivalent is given in parentheses. We have used two-meter glass columns for those methods that call for a nominal six-foot glass column. Two-meter glass columns give more consistent results, through tighter control of the column length and internal diameter, and thus of the volume of chromatographic packing.

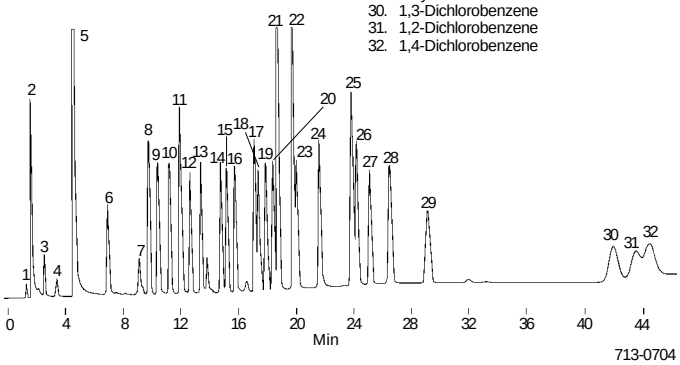
These methods are discussed in detail in the *Federal Register* (2). The chromatographic packings and columns used in these analyses are listed following the method outlines.

GC-MS Method 624 – Volatile Pollutants

Figure A. Volatiles by EPA Method 624

Column: **60/80 Carbopack™ B/1% SP™-1000, 8' x 1/8" OD SS**
Cat. No.: **11815** (15g packing)
Oven: 45°C (3 min) to 220°C at 8°C/min, hold 15 min
Carrier: helium, 40mL/min
Det.: FID, 250°C
Inj.: 1µL dodecane containing 200-500ng/µL each analyte, 200°C

1. Chloromethane
2. Methanol
3. Bromomethane
4. Vinyl chloride & Dichlorofluoromethane
5. Chloroethane
6. Methylene chloride
7. Trichlorofluoromethane
8. 1,1-Dichloroethylene
9. Bromochloromethane (IS)
10. 1,1-Dichloroethane
11. trans-1,2-Dichloroethylene
12. Chloroform
13. 1,2-Dichloroethane
14. 1,1,1-Trichloroethane
15. Carbon tetrachloride
16. Bromodichloromethane
17. 1,2-Dichloropropane
18. trans-1,3-Dichloropropene
19. Trichloroethylene
20. Benzene
21. cis,1,3-Dichloropropene, 1,1,2-Trichloroethane, & Chlorodibromomethane
22. 1-Chloro-2-bromopropane (IS)
23. 2-Chloroethyl vinyl ether
24. Bromoform
25. 1,1,2,2-Tetrachloroethylene & 1,1,2,2-Tetrachloroethane
26. 1,4-Dichlorobutane (IS)
27. Toluene
28. Chlorobenzene
29. Ethylbenzene
30. 1,3-Dichlorobenzene
31. 1,2-Dichlorobenzene
32. 1,4-Dichlorobenzene



713-0704

Sample Concentration

Purge and trap, using a 30.5cm x 0.105" ID x 0.125" OD SS trap containing 15cm Tenax®, 8cm Silica Gel 15, and 1cm 3% SP-2100.

GC Column

6' x 1/8" OD SS containing 60/80 Carbopack B/1% SP-1000. Figure A shows the analysis on an 8' column also used in Method 601. A 2" x 1/8" OD SS precolumn containing 3% SP-1000 on 60/80 Chromosorb® W AW is recommended.

Confirmational Column

8' x 1/8" OD SS containing 60/80 Carbopack C/0.2% CARBOWAX® 1500. A 2" x 1/8" OD SS precolumn containing 3% CARBOWAX 1500 on 60/80 Chromosorb W AW is recommended.

Detector

Mass spectrometer. For Figure A an FID was used to simulate the mass spectrometer analysis.

Qualifications

Acrolein and acrylonitrile are volatile compounds, but purging efficiencies for them are low and erratic. For these compounds, the EPA recommends direct aqueous injection or the modified purge-trap procedure described in EPA Method 603.

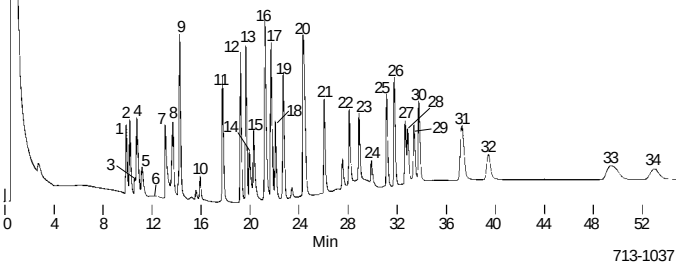
GC-MS Method 625 – Nonvolatile Pollutants

I. Base Neutrals

Figure B. Base-Neutrals by EPA Method 625

Column: **3% SP-2250 on 100/120 SUPELCOPORT™, 2m x 2mm ID glass**
Cat. No.: **11756** (20g packing)
Oven: 50°C (4 min) to 270°C at 8°C/min
Carrier: nitrogen, 30mL/min
Det.: FID
Inj.: 1µL methylene chloride containing 0.125mg/mL or 0.063mg/mL (*) each analyte

1. 1,3-Dichlorobenzene
2. 1,4-Dichlorobenzene
3. bis(2-Chloroethyl)ether
4. Hexachloroethane & 1,2-Dichlorobenzene
5. bis(Methyl-2-chloroethyl)ether
6. N-Nitroso-di-n-propylamine
7. Nitrobenzene & Hexachlorobutadiene
8. 1,2,4-Trichlorobenzene & Isophorone
9. Naphthalene & bis (2-Chloroethoxy)methane
10. Hexachlorocyclopentadiene
11. 2-Chloronaphthalene
12. Acenaphthylene
13. Acenaphthene
14. Dimethylphthalate
15. 2,6-Dinitrotoluene
16. Fluorene & 4-Chlorophenyl phenyl ether
17. 2,4-Dinitrotoluene
18. Diethylphthalate & N-Nitrosodiphenylamine
19. 4-Bromophenyl phenyl ether & Hexachlorobenzene
20. Phenanthrene & Anthracene
21. Di-n-butyl phthalate
22. Fluoranthene*
23. Pyrene*
24. Benzidine
25. Benzyl butyl phthalate
26. bis(2-Ethylhexyl)phthalate
27. Benz(a)anthracene*
28. Chrysene*
29. 3,3'-Dichlorobenzidine
30. Di-n-octyl phthalate
31. Benzo(b)fluoranthene* & Benzo(k)fluoranthene*
32. Benzo(a)pyrene*
33. Indeno(1,2,3-cd)pyrene* & Dibenz(a,h)anthracene*
34. Benzo(ghi)perylene



713-1037

Sample Concentration

Solvent extraction with methylene chloride followed by concentration to 1mL.

GC Column

2m x 2mm ID glass containing 3% SP-2250 on 100/120 SUPELCOPORT.

Confirmational Column

None listed.

Detector

Mass spectrometer. For Figure B an FID was used to simulate the mass spectrometer analysis.

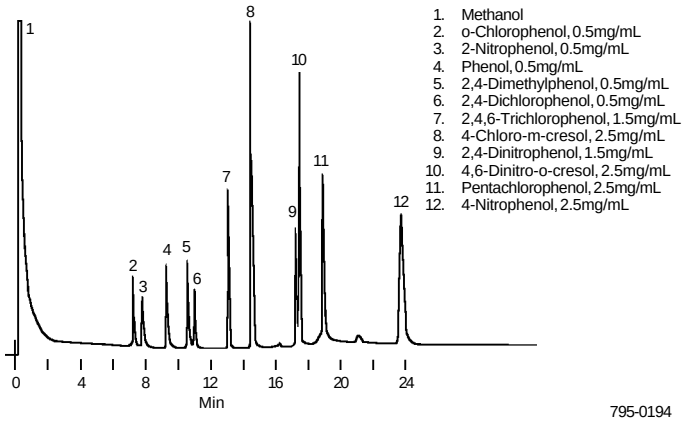
Qualifications

Analysts must be able to chromatograph 100ng of benzidine to demonstrate the inertness of the GC-MS system before they use this procedure on wastewater samples. The EPA has set the detection limit for most of the base-neutrals at 20ng/µL. For 6- and 7-ring polycyclic aromatics, however, the limit is 50ng/µL.

II. Acidics (Phenols)

Figure C. Phenols by EPA Method 625

Column: **1% SP-1240-DA* on 100/120 SUPELCOPORT, 2m x 2mm ID glass**
Cat. No.: **11832** (20g packing)
Oven: 70°C (2 min) to 200°C at 8°C/min, hold
Carrier: helium, 30mL/min
Det.: FID
Inj.: 0.5µL standard phenol mixture (Cat. No. 48810)



795-0194

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL.

GC Column
2m x 2mm ID glass containing 1% SP-1240-DA* on 100/120 SUPELCOPORT.

Confirmational Column
None listed.

Detector
Mass spectrometer. For Figure C an FID was used to simulate the mass spectrometer analysis.

Qualifications
Analysts must chromatograph 50ng of pentachlorophenol to evaluate the inertness of their GC-MS system before they use this method to analyze wastewater samples for phenols.

*DA – Deactivated for acidic compounds.

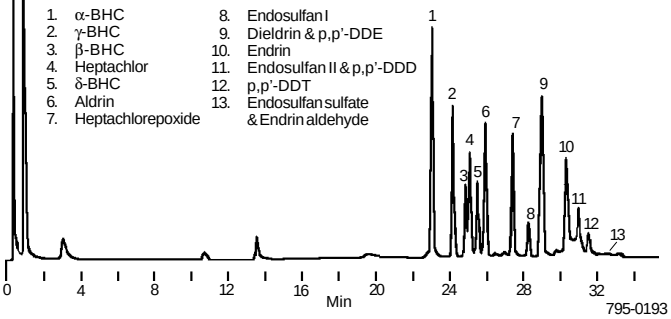
In Method 625, capillary columns may be used as an alternative to packed columns if they meet the QC criteria listed in Sections 8.2, 12, and 13.1 (4). Two available protocols for capillary methodology are 2 & 3 below:

1. *Method of Organic Chemical Analysis of Municipal and Industrial Wastewater* US EPA EMSL, Cincinnati, OH 45268, EPA-600/4-83-057, July 1982.
2. *Testing Methods for Evaluating Solid Waste* US EPA Office of Solid Waste and Emergency Response, Washington, D.C., 20460, SW-846, July, 1982, 2nd Edition.
3. A.D. Sauter, *et al., J. High Resolution Chromatography and Chromatography Communications* **4:** 366 (1981).

III. Pesticides and PCBs

Figure D. Pesticides by EPA Method 625

Column: **3% SP-2250 on 100/120 SUPELCOPORT, 2m x 2mm ID glass**
Cat. No.: **11756** (20g packing)
Oven: 50°C (4 min) to 270°C at 8°C/min
Carrier: nitrogen, 30mL/min
Det.: FID
Inj.: 0.1µL, 1ng/µL each analyte



795-0193

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL. The specific procedure is described in EPA Method 608.

GC Column
2m x 2mm ID glass containing 3% SP-2250 on 100/120 SUPELCOPORT.

Confirmational Column
None listed.

Detector
Mass spectrometer (see **Qualifications**). For Figure D an FID was used to simulate the mass spectrometer analysis.

Qualifications
The sample is analyzed on the GC column with an electron capture detector (ECD) as described in GC Method 608. A GC-MS analysis is performed only if the GC/ECD analysis indicates the presence of pesticides or PCBs.

Pesticides with multiple peaks (PCBs, toxaphene, and chlordane) can be separated from the other pesticides by sample cleanup with Florisil® column chromatography (5).

Analysts must be able to chromatograph 100ng of aldrin before they use the GC-MS procedure on wastewater samples.

Quantification of Priority Pollutants by GC-MS
Internal standards may be used in any of the GC-MS analyses, if they are adequately resolved from the priority pollutants in the sample and from matrix interferences. Two groups of initial standards recommended by the EPA are deuterated and fluorinated compounds of various aromatics, phenols, amines, and nitroaromatics. A mass spectrum of either 4-bromofluorobiphenyl or decafluorotriphenylphosphine must be checked daily to meet performance criteria set forth in Method 625.

If external standards are used to calibrate, individual standards of each compound must be analyzed. A three-point calibration must be performed, with one point of the calibration curve near the limit of detection. The calibration must be verified daily with at least one of the standard solutions used in the initial calibration. If significant variation (±10%) occurs, a new calibration should be conducted.

GC Method 601 – Purgeable Halocarbons

Sample Concentration
Purge and trap, using a 30.5cm x 0.105" ID x 0.125" OD SS trap containing 7.7cm activated charcoal, 7.7cm Silica Gel 15, 7.7cm Tenax, and 1cm 3% SP-2100.

GC Column
8' x 1/8" OD SS containing 60/80 Carbopack B/1% SP-1000.

Confirmational Column
8' x 1/8" OD SS containing n-octane on 80/100 Porasil® C.

Detector
Hall® electroconductivity.

Qualifications
Electron capture detectors are not recommended for this analysis because they have limited sensitivity for mono- and di-substituted halocarbons.

GC Method 602 – Purgeable Aromatics

Sample Concentration
Purge and trap, using a 30.5cm x 0.105" ID x 0.125" OD SS trap containing 1cm 3% SP-2100 and 23cm Tenax.

GC Column
6' x 1/8" OD SS containing 5% SP-1200/1.75% Bentone® 34 on 100/120 SUPELCOPORT.

Confirmational Column
8' x 1/8" OD SS containing 5% 1,2,3-tris(2-cyano-ethoxy) propane on 60/80 Chromosorb W AW.

Detector
Photoionization (10.2 ev lamp). For Figure F an FID was used to simulate the photoionization detector.

Qualifications
FID detection can be used if interfering organics can be resolved from the purgeable aromatics.

GC Method 603 – Acrolein and Acrylonitrile

Sample Concentration
Purge and trap, using a 30.5cm x 0.105" ID x 0.125" OD SS trap containing 1cm 3% SP-2100 and 23cm Tenax.

GC Column
6' x 1/8" OD SS containing Durapak®/Carbowax 400 on 100/120 Porasil C.*

Confirmational Column
6' x 1/8" OD SS containing 80/100 Chromosorb 101.

Detector
FID.

***NOTE:** 100/120 Porasil C is no longer available from the manufacturer.

Figure E. Purgeable Halocarbons by EPA Method 601

Column: **60/80 Carbopack B/1% SP-1000, 8' x 1/8" OD SS**
Cat. No.: **11815** (15g packing)
Oven: 45°C (3 min) to 220°C at 8°C/min, hold 15 min
Carrier: nitrogen, 40mL/min
Det.: Hall, 85°C
Inj.: 1µL dodecane containing 200-500ng/µL each analyte, 200°C

1. Chloromethane
2. Bromomethane
3. Vinyl chloride & Dichlorofluoromethane
4. Chloroethane
5. Methylene chloride
6. Trichlorofluoromethane
7. 1,1-Dichloroethylene
8. Bromochloromethane (IS)
9. 1,1-Dichloroethane
10. trans-1,2-Dichloroethylene
11. Chloroform
12. 1,2-Dichloroethane
13. 1,1,1-Trichloroethane
14. Carbon tetrachloride
15. Bromodichloromethane
16. 1,2-Dichloropropane & trans-1,3-Dichloropropane
17. Trichloroethylene
18. cis-1,3-Dichloropropene, 1,1,2-Trichloroethane, & Chlorodibromomethane
19. 1-Chloro-2-bromopropane (IS)
20. 2-Chloroethyl vinyl ether
21. Bromoform
22. 1,1,2,2-Tetrachloroethylene & 1,1,2,2-Tetrachloroethane
23. 1,4-Dichlorobutane (IS)
24. Chlorobenzene

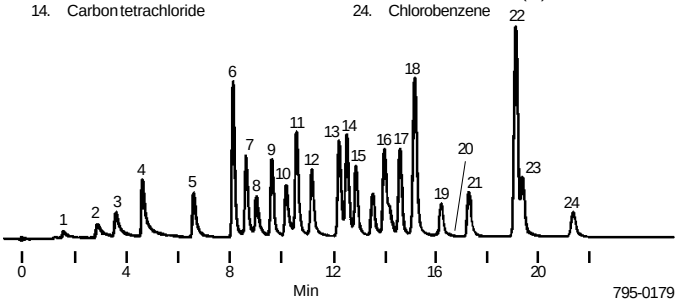


Figure F. Purgeable Aromatics by EPA Method 602

Column: **5% SP-1200/1.75% Bentone 34 on 100/120 SUPELCOPORT, 6' x 1/8" SS**
Cat. No.: **12134** (20g packing)
Oven: 50°C (2 min) to 90°C at 6°C/min, hold
Carrier: helium, 36mL/min
Det.: FID
Inj.: 1µL methanol containing 0.2mg/mL each analyte

1. Benzene
2. Toluene
3. Ethylbenzene
4. Chlorobenzene
5. 1,4-Dichlorobenzene
6. 1,3-Dichlorobenzene
7. 1,2-Dichlorobenzene

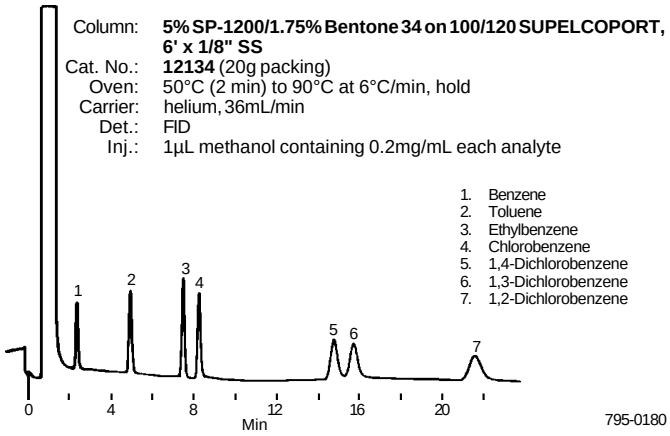
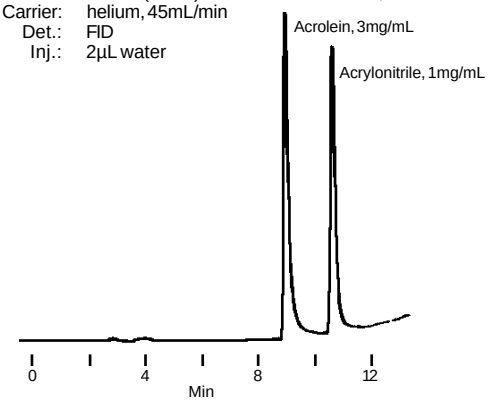


Figure G. Acrolein and Acrylonitrile by EPA Method 603

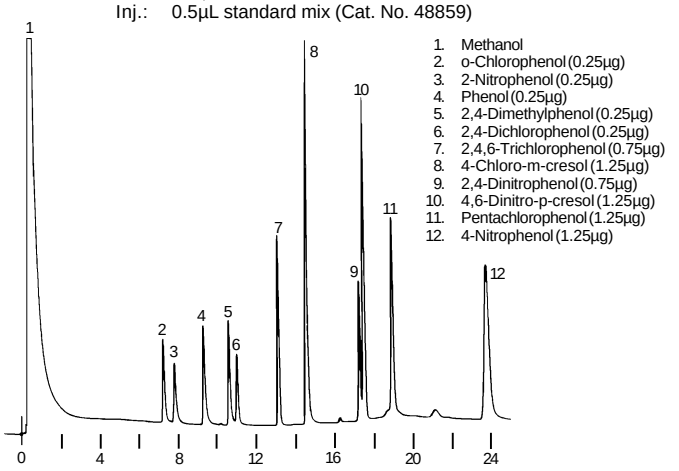
Column: **80/100 Chromosorb 101, 6' x 1/8" OD SS**
Cat. No.: **20214** (50g packing)
Oven: 100°C (5 min) to 140°C at 10°C/min, hold
Carrier: helium, 45mL/min
Det.: FID
Inj.: 2µL water



GC Method 604 – Phenols

Figure H. Phenols by EPA Method 604

Column: **1% SP-1240-DA* on 100/120 SUPELCOPORT, 2m x 2mm ID glass**
Cat. No.: **11832** (20g packing)
Oven: 70°C (2 min) to 200°C at 8°C/min, hold
Carrier: helium, 30mL/min
Det.: FID, 250°C
Inj.: 0.5µL standard mix (Cat. No. 48859)



1. Methanol
2. o-Chlorophenol (0.25µg)
3. 2-Nitrophenol (0.25µg)
4. Phenol (0.25µg)
5. 2,4-Dimethylphenol (0.25µg)
6. 2,4-Dichlorophenol (0.25µg)
7. 2,4,6-Trichlorophenol (0.75µg)
8. 4-Chloro-m-cresol (1.25µg)
9. 2,4-Dinitrophenol (0.75µg)
10. 4,6-Dinitro-p-cresol (1.25µg)
11. Pentachlorophenol (1.25µg)
12. 4-Nitrophenol (1.25µg)

713-1032

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL.

GC Column (Free Phenols)
2m x 2mm ID glass containing 1% SP-1240-DA* on 100/120 SUPELCOPORT. The analysis is similar to the GC-MS analysis in Figure C.

Confirmational Column
None listed.

Detector
FID.

Qualifications
When sample cleanup is required, the extracted phenols are derivatized with pentafluorobenzylbromide (PFB) and the extract is cleaned by silica gel column chromatography. PFB phenols are separated on a column different from that used to separate free phenols, and are detected by electron capture.

GC Column (Derivatized Phenols)
1.8m x 2mm ID glass containing 5% OV®-17 on 80/100 Chromosorb W AW-DMCS. (Supelco Equivalent: 5% SP-2250 on 80/100 SUPELCOPORT.)

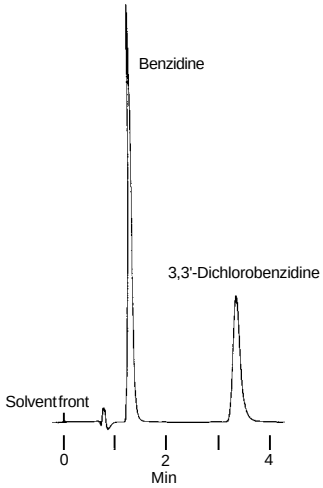
Detector
Electron capture detector.

*DA – Deactivated for acidic compounds.

HPLC Method 605 – Benzidine and 3,3'-Dichlorobenzidine

Figure I. Benzidines by EPA Method 605

Column: **SUPELCOSIL™ LC-1, 5cm x 4.6mm, 5µm particles**
Cat. No.: **58237**
Mobile Phase: 0.1M acetate buffer:acetonitrile, 60:40
Flow Rate: 0.8mL/min
Det.: UV, 254nm
Inj.: 10µL mobile phase containing 0.5µg each analyte



797-0651

Sample Concentration
Solvent extraction with chloroform followed by concentration to 1mL.

HPLC Column
25cm x 4.6mm ID SS containing LiChrosorb® RP-2. (Supelco Column: 25cm x 4.6mm ID SS containing SUPELCOSIL LC-1).

Confirmational Column
None listed.

Detector
Electrochemical (0.8 volts). For Figure I, UV detection at 254nm was used (see **Qualifications**).

Qualifications
A UV detector may be used if there are no matrix interferences.

The EPA procedure suggests using a 25cm x 4.6mm ID column, but a more than adequate separation is readily achieved with a 5cm x 4.6mm ID or a 15cm x 4.6mm ID SUPELCOSIL LC-1 column.

GC Method 606 – Phthalate Esters

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL.

GC Column
2m x 4mm ID glass containing 1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT. Two temperatures, 180°C and 220°C, are used.

Confirmational Column
2m x 4mm ID glass containing 3% OV-1 on 100/120 SUPELCOPORT. (Supelco Equivalent: 3% SP-2100 on 100/120 SUPELCOPORT.)

Detector
Electron capture detector.

Qualifications
If the extract must be cleaned, the EPA recommends Florisil or silica gel column chromatography.

GC Method 607 – Nitrosamines

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL.

GC Column
2m x 4mm ID glass containing 10% CARBOWAX 20M/2% KOH on 80/100 Chromosorb W AW. Two temperatures, 110°C and 220°C, are used.

Confirmational Column
2m x 4mm ID glass containing 10% SP-2250 on 100/120 SUPELCOPORT.

Detector
Nitrogen-phosphorous detector. For Figure K an FID was used in place of a nitrogen-phosphorous detector.

Qualifications
N-Nitrosodiphenylamine decomposes in the GC injection port and is detected as diphenylamine. Therefore, diphenylamine in the sample must be removed by Florisil column chromatography or it will interfere with the analysis.

GC Method 608 – Organochlorine Pesticides and PCBs

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL.

GC Column
2m x 4mm ID glass containing 1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT.

Confirmational Column
2m x 2mm ID glass containing 3% OV-1 on 100/120 SUPELCOPORT. (Supelco Equivalent: 3% SP-2100 on 100/120 SUPELCOPORT.)

Detector
Electron capture detector.

Qualifications
The extract must be cleaned by Florisil column chromatography to eliminate possible phthalate interference (5).

Figure J. Phthalates by EPA Method 606

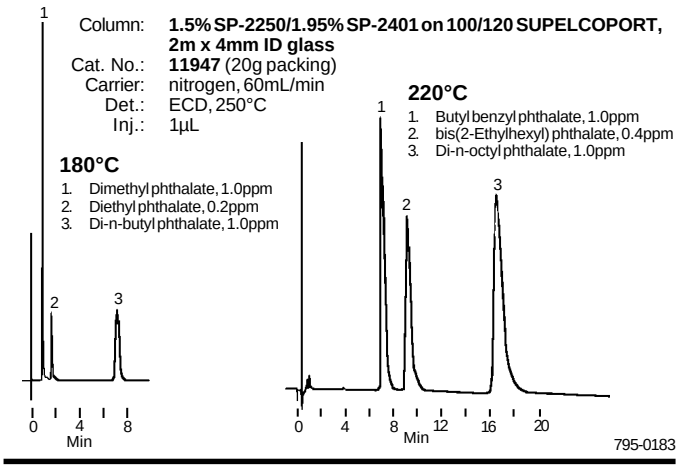


Figure K. Nitrosamines by EPA Method 607

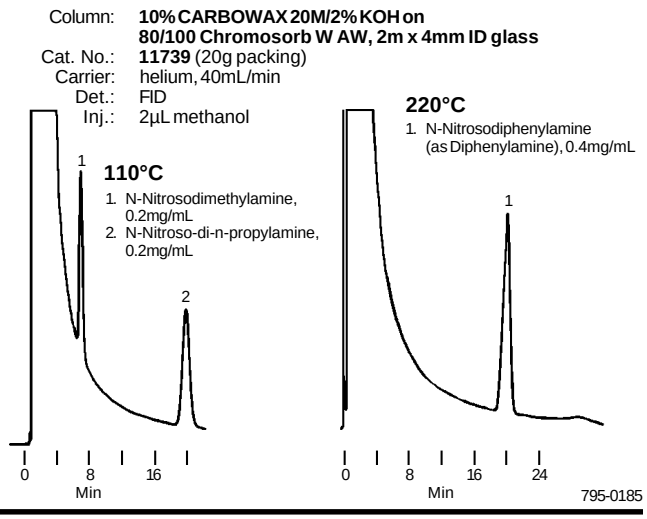
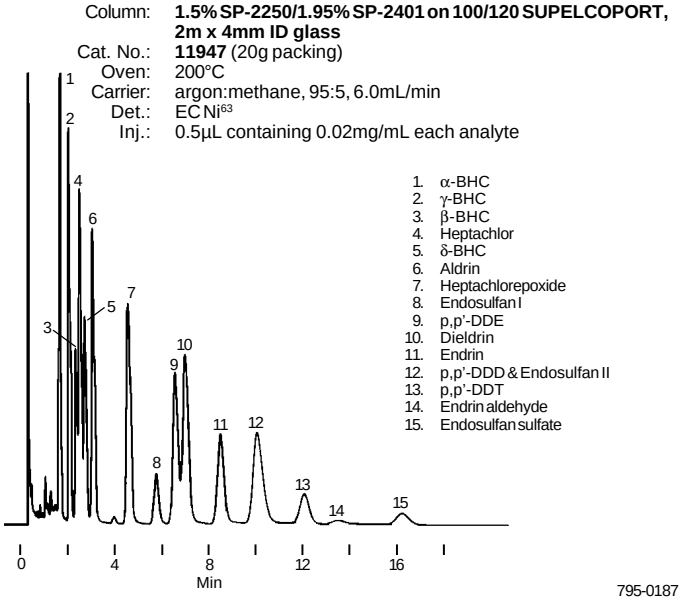


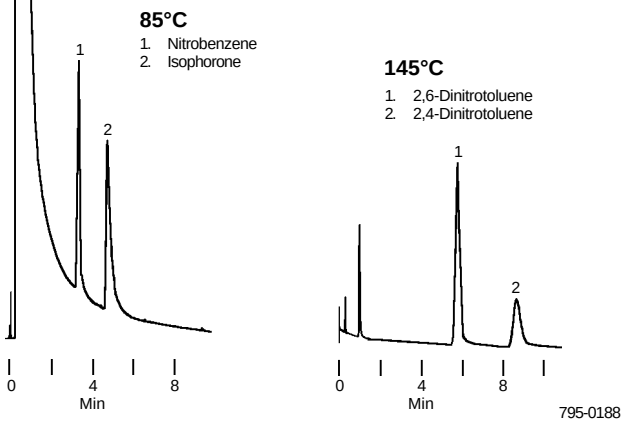
Figure L. Pesticides by EPA Method 608



GC Method 609 – Nitroaromatics and Isophorone

Figure M. Nitroaromatics and Isophorone by EPA Method 609

Column: **1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT, 2m x 4mm ID glass**
Cat. No.: **11947** (20g packing)
Carrier: nitrogen, 44mL/min
Det.: FID (nitrobenzene, isophorone) or ECD (dinitrotoluenes)
Inj.: 2µL, 0.2mg/mL each analyte (nitrobenzene, isophorone) or 0.5µL, 2ng/µL each analyte (dinitrotoluenes)



795-0188

Sample Concentration

Solvent extraction with methylene chloride followed by concentration to 1mL.

GC Column

4' x 4m ID glass containing 1.95% QF-1/1.5% OV-17 on 80/100 Gas-Chrom® Q. (Supelco Equivalent: 2m x 4mm ID glass containing 1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT.) Two temperatures, 85°C and 145°C, are used.

Confirmational Column

10' x 4mm ID glass containing 3% OV-101 on 80/100 Gas-Chrom Q. (Supelco Equivalent: 3% SP-2100 on 100/120 SUPELCOPORT.)

Detector

FID for isophorone and nitrobenzene; electron capture detector for nitrotoluenes.

Qualifications

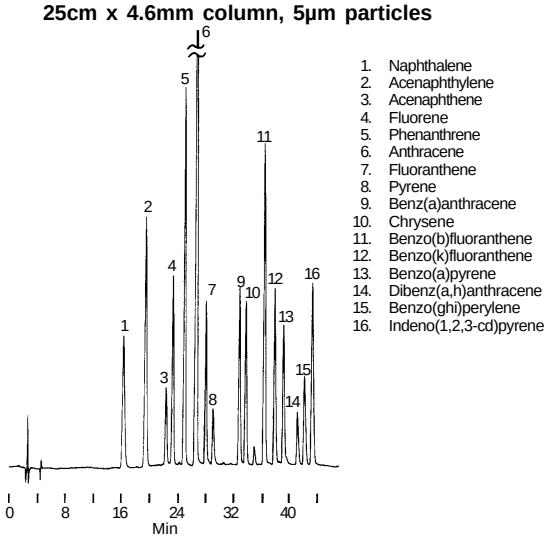
The Supelco equivalent column is two meters long, rather that four feet long, to permit its application to Methods 606, 608, and 613.

GC or LC Method 610 – Polynuclear Aromatic Hydrocarbons (PAHs)

Figure N. PAHs by HPLC by EPA Method 610

Columns: **SUPELCOSIL LC-PAH**
Cat. No.: **58229** (top) or **59133**
Mobile Phase: water (A):acetonitrile (B) gradient
top – 40% B (5 min) to 100% B over 25 min, hold
bottom – 60% B (0.3 min) to 100% B over 2.7 min, hold 1 min
Flow Rate: 1mL/min (top) or 3.0mL/min
Det.: UV, 254nm
Inj.: 2µL methanol/methylene chloride containing 0.4µg each analyte

25cm x 4.6mm column, 5µm particles



5cm x 4.6mm column, 3µm particles

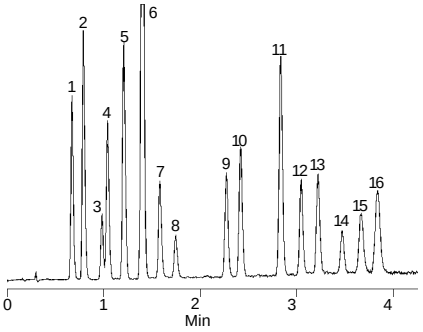


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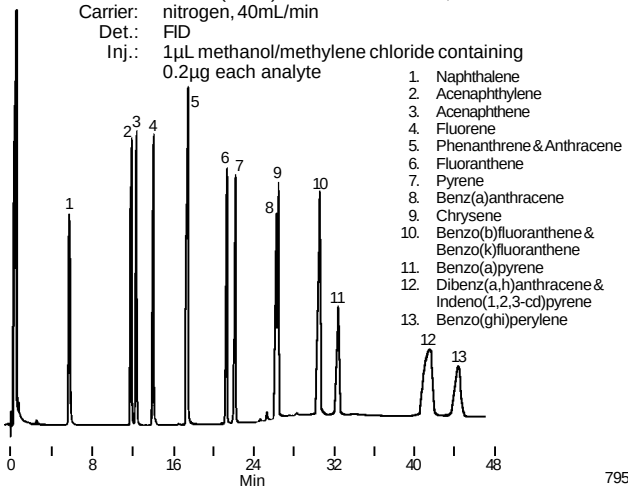
Figure O. PAHs by GC by EPA Method 610

Column: **3% SP-2250 on 100/120 SUPELCOPORT, 2m x 2mm ID glass**
Cat. No.: **11744** (20g packing)
Oven: 100°C (4 min) to 280°C at 8°C/min, hold
Carrier: nitrogen, 40mL/min
Det.: FID
Inj.: 1µL methanol/methylene chloride containing 0.2µg each analyte



795-0189

Method 610 (contd.)

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL.

HPLC Column
25cm x 4.6mm ID SS containing HC-ODS Sil-X reversed phase. (Supelco Equivalent: 25cm x 4.6mm ID SS containing SUPELCOSIL LC-PAH.)

Confirmational Column
None listed.

Detector
Fluorescence.

GC Column
2m x 2mm ID glass containing 3% OV-17 on 100/120 Chromosorb W AW-DMCS. (Supelco Equivalent: 3% SP-2250 on 100/120 SUPELCOPORT.)

Confirmational Column
None listed.

Detector
FID.

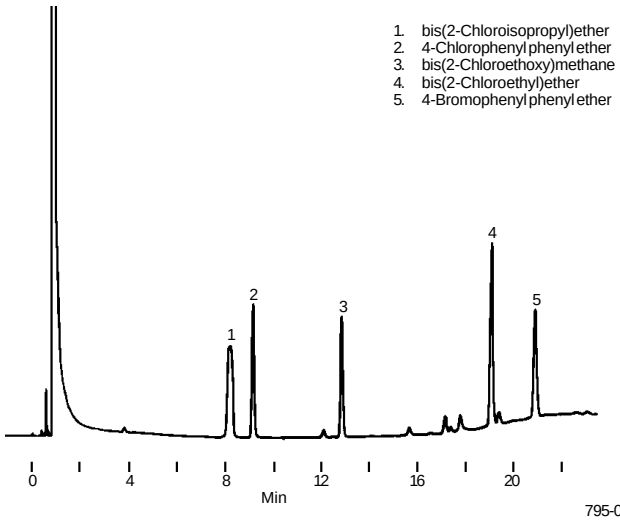
Qualifications
The HPLC procedure is recommended for complete resolution of the PAHs; the GC procedure cannot adequately resolve four pairs of these compounds. The EPA method suggests using a 25cm x 4.6mm ID HPLC column containing 5µm packing particles for this analysis, but shorter SUPELCOSIL LC-PAH columns (15cm x 4.6mm ID, 5µm particles or 5cm x 4.6mm ID, 3µm particles) can greatly reduce the analysis time, as Figure N shows.

GC Method 611 – Haloethers

Figure P. Haloethers by EPA Method 611

Column: **3% SP-1000 on 100/120 SUPELCOPORT, 2m x 2mm ID glass**
Cat. No.: **11746** (20g packing)
Oven: 60°C (2 min) to 230°C at 8°C/min, hold
Carrier: helium, 40mL/min
Det.: FID
Inj.: 1µL methanol containing 0.2mg/mL each analyte

1. bis(2-Chloroisopropyl)ether
2. 4-Chlorophenyl phenyl ether
3. bis(2-Chloroethoxy)methane
4. bis(2-Chloroethyl)ether
5. 4-Bromophenyl phenyl ether



795-0190

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL

GC Column
2m x 2mm ID glass containing 3% SP-1000 on 100/120 SUPELCOPORT.

Confirmational Column
2m x 2mm ID glass containing 60/80 Tenax.

Detector
Hall electroconductivity. An FID was used to obtain Figure P.

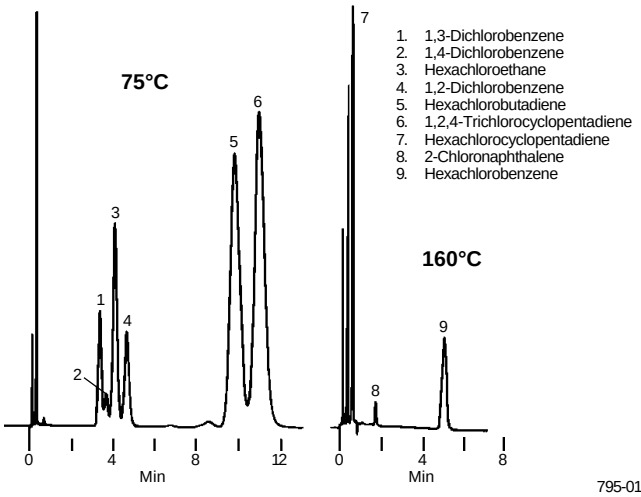
Qualifications
The sample should be cleaned on Florisil if interferences are suspected to exist in the sample.

GC Method 612 – Chlorinated Hydrocarbons

Figure Q. Chlorinated Hydrocarbons by EPA Method 612

Column: **1.5% OV-1/1.5% OV-225 on 80/100 SUPELCOPORT, 2m x 2mm ID glass**
Cat. No.: custom-prepared
Carrier: argon:methane, 95:5, 30mL/min
Det.: ECD
Inj.: 2µL hexane containing 0.1-10ng/µL each analyte

1. 1,3-Dichlorobenzene
2. 1,4-Dichlorobenzene
3. Hexachloroethane
4. 1,2-Dichlorobenzene
5. Hexachlorobutadiene
6. 1,2,4-Trichlorocyclopentadiene
7. Hexachlorocyclopentadiene
8. 2-Chloronaphthalene
9. Hexachlorobenzene



795-0191

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL.

GC Column
2m x 2mm ID glass containing 1.5% OV-1/2.4% OV-225 on 80/100 SUPELCOPORT (replaces 1.5% OV-1/1.5% OV-225 packing used for Figure Q.) Two temperatures, 75°C and 160°C, are used.

Confirmational Column
None listed.

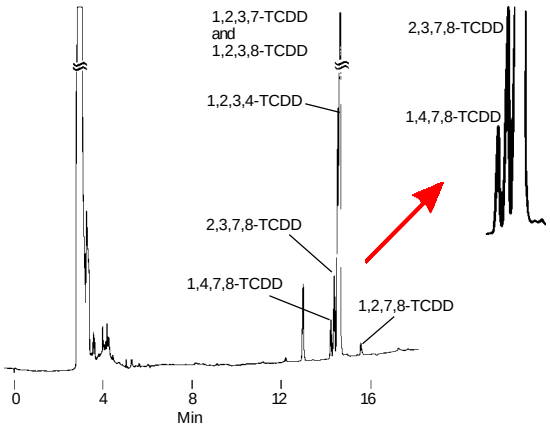
Detector
Electron capture detector.

Qualifications
Sample cleanup, if required, is conducted on a Florisil column.

GC Method 613 – 2,3,7,8-Tetrachlorobenzo-p-dioxin (TCDD)

Figure R. 2,3,7,8-TCDD and Other TCDD Isomers by EPA Method 613

Column: **SP-2331 capillary column, 60m x 0.32mm ID, 0.2µm film**
Cat. No.: **24105**
Oven: 200°C (1 min) to 250°C at 3°C/min
Carrier: helium, 30cm/sec
Det.: ECD
Inj.: 0.2µL n-dodecane containing 0.2ng each isomer, splitless injection, 250°C



713-1065

Sample Concentration
Solvent extraction with methylene chloride followed by concentration to 1mL. The sample is cleaned on a silica gel column, then on an alumina column.

GC Column
60m x 0.32mm ID capillary column containing SP-2331.

Detector
Mass spectrometer.

Qualifications
A separate method was established for TCDD analysis because of the extreme toxicity of this compound. This method should be reviewed thoroughly before it is used.

A 60m x 0.32mm ID capillary column containing SP-2331 resolves 2,3,7,8-TCDD from other TCDD isomers. For additional information on this analysis, request Application Note 113.

Quantification of Priority Pollutants by GC or LC
The EPA also has recommended calibration procedures for the GC or LC analyses of priority pollutants. Prior to any calibration, the chromatographer must demonstrate that the system is operational by injecting a known mixture of the components to be analyzed.

A blank containing all reagents used is carried through the extraction and cleanup procedures and is analyzed to ensure the absence of interferences. Concentrations of calibration standards are chosen to bracket the expected concentration of the compound in the sample. These standards establish the sensitivity limit of the detector and the linear range of the analytical system for each component.

Once a graph of the standard concentrations vs. response is established, it is checked daily to ensure that no significant variation has occurred in the standard curve. Many of the methods recommend that surrogate standards be included in all standards, samples, and blanks for evaluation of the recovery and precision of the sample workup and analysis. If doubt exists about the identity of a peak in the chromatographic analysis, mass spectrometry should be used for confirmation.

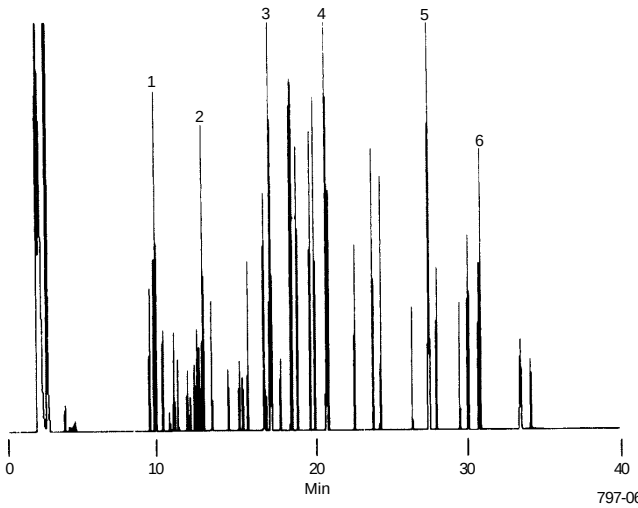
Internal standards, surrogates, and calibration standards required in the GC-MS or the GC or LC methods are listed in the chemical standards section of the Supelco catalog.

Use a Capillary Column to Analyze Difficult or Complex Samples
In US EPA Method 625, capillary columns may be used as an alternative to packed columns if they meet the QC criteria listed in Sections 8.2, 12, and 13.1 (see page 3). 0.25mm ID, 0.32mm ID, and 0.53mm ID SPB™-5 capillary columns provide similar resolution of acid and base/neutral pollutants for Method 625 (Figure S). In addition, you can use 0.53mm ID columns in packed column chromatographs. In a GC-MS system with a high capacity pump or jet separator, a 0.53mm ID column combines large sample capacity (up to 2000ng/component) with rapid analysis and good resolution.

Figure S. Acid and Base/Neutral Pollutants

Column: **PTE™-5 capillary column, 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24135-U**
Oven: 35°C (4 min) to 300°C at 10°C/min, hold 10 min
Carrier: helium, 40cm/sec (set at 250°C)
Det.: MS (mass range: 35-450 m/z; 1.18 sec/scan)

N-Nitrosodimethylamine
Phenol
2-Chlorophenol
bis(2-Chloroethyl) ether
1,3-Dichlorobenzene
1. 1,4-Dichlorobenzene-d_4
1,4-Dichlorobenzene
1,2-Dichlorobenzene
bis(2-Chloroisopropyl) ether
Hexachloroethane
N-Nitroso-di-n-propylamine
Nitrobenzene
Isophorone
2-Nitrophenol
2,4-Dimethylphenol
bis(2-Chloroethoxy)methane
2,4-Dichlorophenol
1,2,4-Trichlorobenzene
2. Naphthalene-d_8
Naphthalene
Hexachlorobutadiene
p-Chloro-m-cresol
Hexachlorocyclopentadiene
2,4,6-Trichlorophenol
2-Chloronaphthalene
Acenaphthylene
Dimethylphthalate
2,6-Dintrotoluene
3. Acenaphthene-d_{10}
Acenaphthene
2,4-Dinitrophenol
4-Nitrophenol
2,4-Dinitrotoluene
Diethyl phthalate
Fluorene
4-Chlorophenylphenyl ether
4,6-Dinitro-o-cresol
N-Nitrosodiphenylamine
1,2-Diphenylhyrazine
4-Bromophenylphenyl ether
Hexachlorobenzene
Pentachlorophenol
4. Phenanthrene-d_{10}
Phenanthrene
Anthracene
Di-n-butyl phthalate
Fluoranthene
Benzidine
Pyrene
Benzyl butyl phthalate
Benzo(a)anthracene
3,3'-Dichlorobenzidine
5. Chrysene-d_{12}
Chrysene
bis(2-Ethylhexyl)phthalate
Di-n-octyl phthalate
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
6. Indeno(1,2,3-cd)pyrene
Dibenzo(a,h)anthracene
Benzo(ghi)perylene

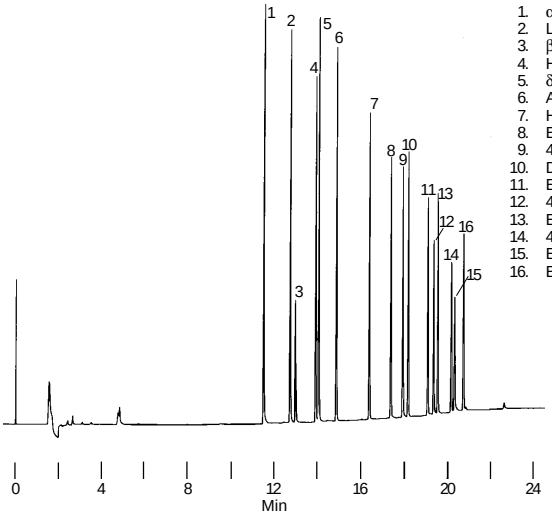


797-0665

0.25mm ID and 0.53mm ID SPB-608 capillary columns offer excellent resolving power and inertness for separating the pesticides listed in US EPA Method 608 (Figure T). In addition to routine testing for efficiency and inertness, each SPB-608 column is tested to ensure minimal breakdown of DDT and endrin, as required by the EPA method. Furthermore, you can use a 0.53mm ID column in instruments designed for packed columns.

Figure T. Chlorinated Pesticides

Column: **SPB-608 capillary column, 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24103-U**
Oven: 150°C (4 min) to 290°C at 8°C/min, hold 5 min
Carrier: helium, 25cm/sec (set at 290°C*)
Det.: ECD
Inj.: 0.8µL decane containing 160pg each analyte, splitless injection, 45 sec hold time



1. α-BHC
2. Lindane (γ-BHC)
3. β-BHC
4. Heptachlor
5. δ-BHC
6. Aldrin
7. Heptachlor epoxide
8. Endosulfan I
9. 4,4'-DDE
10. Dieldrin
11. Endrin
12. 4,4'-DDD
13. Endosulfan II
14. 4,4'-DDT
15. Endrin aldehyde
16. Endosulfan sulfate

796-0056

*A halogenated gas such as chloromethane or chlorotrifluoromethane is used to determine linear velocity by ECD.

Wide Bore Capillary Columns Are Compatible with Purge and Trap Devices

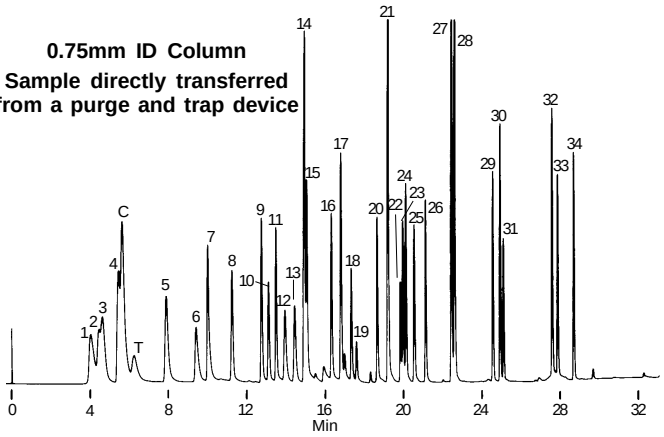
Our 0.53mm ID and 0.75mm ID VOCOL™ columns are specifically manufactured and tested to rapidly separate the volatile pollutants listed in EPA Methods 601, 602, and 624 for wastewater (Figure U) and 502.2 and 524.2 for drinking water. Because these columns have high optimum carrier gas flow rates, they accept samples directly from purge and trap devices. VOCOL columns are compatible with less sensitive detectors and concentration-dependent hyphenated techniques, such as GC-FTIR. The 0.53mm ID columns have a capacity of about 2000ng/sample component; the 0.75mm ID columns have a capacity of about 10,000ng/component.

Figure U. Volatile Priority Pollutants

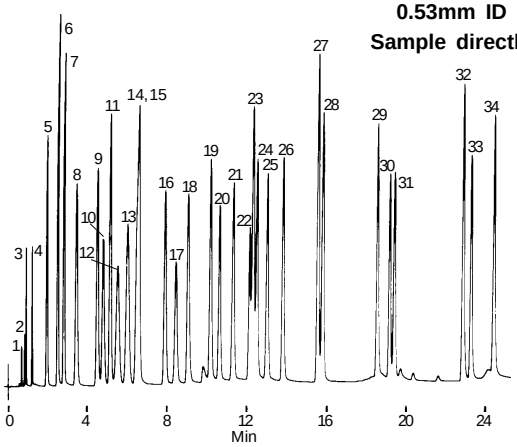
Columns: **VOCOL capillary columns, 60m x 0.75mm ID, 1.5µm film** (top) **or 30m x 0.53mm ID, 3.0µm film**
Cat. No.: **25320-U** (bottom)
Oven: 10°C (6 min) to 170°C at 6°C/min (top) or 35°C (4 min) to 190°C at 4°C/min
Carrier: helium, 10mL/min
Det.: FID

1. Dichlorodifluoromethane
2. Chloromethane
3. Vinyl chloride
4. Bromomethane
C. Chloromethane (when present)
T. Trichlorofluoromethane (when present)
5. 1,1-Dichloroethylene
6. Methylene chloride
7. trans-1,2-Dichloroethylene
8. 1,1-Dichloroethane
9. cis-1,2-Dichloroethylene
10. Chloroform
11. Bromochloromethane
12. 1,1,1-Trichloroethane
13. Carbon tetrachloride
14. Benzene
15. 1,2-Dichloroethane
16. Trichloroethylene
17. 1,2-Dichloropropane
18. Bromodichloromethane
19. 2-Chloroethyl vinyl ether
20. cis-1,3-Dichloropropene
21. Toluene
22. trans-1,3-Dichloropropene
23. 1-Chloro-2-bromopropane
24. 1,1,2-Trichloroethane
25. Tetrachloroethylene
26. Dibromochloromethane
27. Chlorobenzene
28. Ethylbenzene
29. Bromoform
30. 1,4-Dichlorobutane
31. 1,1,2,2-Tetrachloroethane
32. 1,3-Dichlorobenzene
33. 1,4-Dichlorobenzene
34. 1,2-Dichlorobenzene

0.75mm ID Column
Sample directly transferred from a purge and trap device



0.53mm ID Column
Sample directly injected



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Ordering Information:

Packings and Columns for USEPA Wastewater Analyses

For chemical standards for these methods, refer to the current Supelco catalog.

EPA Method No.	Class of Pollutants	Packings and Columns	Cat. No.
Gas or Liquid Chromatography			
601	Purgeable Halocarbons	60/80 Carbopack B/1% SP-1000, 15g	**11815**
		Packing for Confirmation Column:	
		n-Octane on 80/100 Porasil C, 75cc	**11733-U**
		Capillary GC Columns:	
		VOCOL, 60m x 0.75mm ID glass	NA*
		VOCOL, 30m x 0.53mm ID fused silica	**25320-U**
602	Purgeable Aromatics	5% SP-1200/1.75% Bentone 34 on 100/120 SUPELCOPORT, 20g	**12134**
		Packing for Confirmation Column:	
		5% 1,2,3-TCEP on 60/80 Chromosorb W AW, 20g	**11765-U**
		Capillary GC Columns:	
		VOCOL, 60m x 0.75mm ID glass	NA*
		VOCOL, 30m x 0.53mm ID fused silica	**25320-U**
603	Acrolein & Acrylonitrile	80/100 Porapak QS, 24g	**20343**
		Packing for Confirmation Column:	
		80/100 Chromosorb 101, 50g	**20214**
604	Phenols	*Free Phenols:*	
		1% SP-1240-DA on 100/120 SUPELCOPORT, 20g	**11832**
		Derivatives:	
		5% SP-2250 on 80/100 SUPELCOPORT, 20g	**11737**
		Capillary GC Column:	
		SPB-5, 15m x 0.53mm ID fused silica	**25304**
605	Benzidines	*HPLC Column:*	
		SUPELCOSIL LC-1, 25cm x 4.6mm	**58296**
		Capillary GC Column:	
		SPB-5, 15m x 0.53mm ID fused silica	**25304**
606	Phthalates	1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT, 20g	**11947**
		Packing for Confirmation Column:	
		3% SP-2100 on 100/120 SUPELCOPORT, 20g	**11738**
		Capillary GC Column:	
		SPB-5, 15m x 0.53mm ID fused silica	**25304**
607	Nitrosamines	10% CARBOWAX 20M/2% KOH on 80/100 Chromosorb W AW, 20g	**11739**
		Capillary GC Column:	
		SPB-5, 15m x 0.53mm ID fused silica	**25304**
608	Organochlorine Pesticides & PCBs	1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT, 20g	**11947**
		Packing for Confirmation Column:	
		3% SP-2100 on 100/120 SUPELCOPORT, 20g	**11738**
		Capillary GC Columns:	
		SPB-608, 30m x 0.25mm ID fused silica	**24103-U**
		SPB-608, 15m x 0.53mm ID fused silica	**25310-U**
609	Nitroaromatics & Isophorone	1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT, 20g	**11947**
		Packing for Confirmation Column:	
		3% SP-2100 on 100/120 SUPELCOPORT, 20g	**11738**
		Capillary GC Column:	
		SPB-5, 15m x 0.53mm ID fused silica	**25304**
610	PAHs	3% SP-2250 on 100/120 SUPELCOPORT, 20g	**11744**
		HPLC Column:	
		SUPELCOSIL LC-PAH, 25cm x 4.6mm	**58229**
		Capillary GC Column:	
		SPB-5, 30m x 0.53mm ID fused silica	**25305-U**
611	Haloethers	3% SP-1000 on 100/120 SUPELCOPORT, 20g	**11746**
		Capillary GC Column:	
		SPB-5, 15m x 0.53mm ID fused silica	**25304**

Packings and Columns for USEPA Wastewater Analyses (contd.)

EPA Method No.	Class of Pollutants	Packings and Columns	Cat. No.
612	Chlorinated Hydrocarbons	1.5% OV-1/2.4% OV-225 on 80/100 SUPELCOPORT	**custom**
		Capillary GC Column:	
		SPB-5, 15m x 0.53mm ID fused silica	**25304**
613	2,3,7,8-TCDD	*Capillary GC Columns:*	
		SP-2331, 60m x 0.25mm ID fused silica	**24104-U**
		SP-2331, 60m x 0.32mm ID fused silica	**24105**
GC/MS Methods			
624	Purgeable Halocarbons	60/80 Carbopack B/1% SP-1000, 15g	**11815**
		Packing for Confirmation Column:	
		60/80 Carbopack C/0.2% CARBOWAX 1500, 15g	**11826**
		Packing for Precolumn:	
		3% SP-1000 on 60/80 Chromosorb W AW, 20g	**11741**
		Capillary GC Columns:	
		VOCOL, 60m x 0.75mm ID glass	NA*
		VOCOL, 30m x 0.53mm ID fused silica	**25320-U**
625	Acids (Phenols), Base-Neutrals, Organochlorine Pesticides, PCBs	3% SP-2250 on 100/120 SUPELCOPORT, 20g	**11756**
		Acids:	
		1% SP-1240-DA on 100/120 SUPELCOPORT, 20g	**11832**
		Acids, Base-Neutrals, Organochlorine Pesticides, PCBs:	
		PTE-5, 30m x 0.25mm ID fused silica (0.25µm phase film)	**24135-U**

*No longer available; we recommend a 0.53mm ID fused silica column for this application.

For chemical standards for these methods, refer to the current Supelco catalog.

References

1. *Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants* USEPA Effluent Guidelines Division, Washington (April, 1977).
2. *Federal Register* Vol. 44, No. 233, Dec. 3, 1979.
3. *Federal Register* Vol. 45, No. 98, May 19, 1980.
4. Bellar, T.A., and J.J. Lichtenberg, *J. Am. Water Works Assoc.,* **66:** 739-744 (1974).
5. *Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples* EPA-600/8-80-038, USEPA, Health Effects Research Laboratory,Research Triangle Park, NC (1980).

References not available from Supelco.

Trademarks

Carbopack, PTE, SP, SPB, SUPELCOPORT, SUPELCOSIL, VOCOL – Sigma-Aldrich Co.
Bentone – National Lead Company, Baroid Sales Division
CARBOWAX – Union Carbide Corporation
Chromosorb – Celite Corp.
Durapak, Porapak, Porasil – Waters Associates, Inc.
Florisil – U.S. Silica Co.
Gas-Chrom – Applied Science Laboratories, Inc.
LiChrosorb – EM Laboratories, Inc.
OV – Ohio Valley Specialty Chemical Company
Tenax – Enka Research Institute Arnhem

Fused silica columns manufactured under HP US patent no. 4,293,415.