METHOD 8250

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS: PACKED COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8250 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications.

1.2 Method 8250 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic packed column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected and are not being determined by Method 8080. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The practical quantitation limit (PQL) of Method 8250 for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 ug/L for ground water samples (see Table 2). PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

TABLE 1. CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Method detection limit (ug/L)	Primary Ion	Secondary Ion(s)
Acenaphthene	17.8	1.9	154	153, 152
Acenaphthene-d_{10} (I.S.)	--	--	164	162, 160
Acenaphthylene	17.4	3.5	152	151, 153
Acetophenone	--	--	105	77, 51
Aldrin	24.0	1.9	66	263, 220
Aniline	--	--	93	66, 65
Anthracene	22.8	1.9	178	176, 179
4-Aminobiphenyl	--	--	169	168, 170
Aroclor-1016[b]	18-30	--	222	260, 292
Aroclor-1221[b]	15-30	30	190	224, 260
Aroclor-1232[b]	15-32	--	190	224, 260
Aroclor-1242[b]	15-32	--	222	256, 292
Aroclor-1248[b]	12-34	--	292	362, 326
Aroclor-1254[b]	22-34	36	292	362, 326
Aroclor-1260[b]	23-32	--	360	362, 394
Benzidine[a]	28.8	44	184	92, 185
Benzoic acid	--	--	122	105, 77
Benzo(a)anthracene	31.5	7.8	228	229, 226
Benzo(b)fluoranthene	34.9	4.8	252	253, 125
Benzo(k)fluoranthene	34.9	2.5	252	253, 125
Benzo(g,h,i)perylene	45.1	4.1	276	138, 277
Benzo(a)pyrene	36.4	2.5	252	253, 125
Benzyl alcohol	--	--	108	79, 77
α-BHC[a]	21.1	--	183	181, 109
β-BHC	23.4	4.2	181	183, 109
δ-BHC	23.7	3.1	183	181, 109
γ-BHC (Lindane)[a]	22.4	--	183	181, 109
Bis(2-chloroethoxy)methane	12.2	5.3	93	95, 123
Bis(2-chloroethyl)ether	8.4	5.7	93	63, 95
Bis(2-chloroisopropyl)ether	9.3	5.7	45	77, 121
Bis(2-ethylhexyl)phthalate	30.6	2.5	149	167, 279
4-Bromophenyl phenyl ether	21.2	1.9	248	250, 141
Butyl benzyl phthalate	29.9	2.5	149	91, 206
Chlordane[b]	19-30	--	373	375, 377
4-Chloroaniline	--	--	127	129
1-Chloronaphthalene	--	--	162	127, 164
2-Chloronaphthalene	15.9	1.9	162	127, 164
4-Chloro-3-methylphenol	13.2	3.0	107	144, 142
2-Chlorophenol	5.9	3.3	128	64, 130
4-Chlorophenyl phenyl ether	19.5	4.2	204	206, 141
Chrysene	31.5	2.5	228	226, 229
Chrysene-d_{12} (I.S.)	--	--	240	120, 236
4,4'-DDD	28.6	2.8	235	237, 165
4,4'-DDE	27.2	5.6	246	248, 176

TABLE 1. - Continued

Compound	Retention Time (min)	Method detection limit (ug/L)	Primary Ion	Secondary Ion(s)
4,4'-DDT	29.3	4.7	235	237, 165
Dibenz(a,j)acridine	--	--	279	280, 277
Dibenz(a,h)anthracene	43.2	2.5	278	139, 279
Dibenzofuran	--	--	168	139
Di-n-butylphthalate	24.7	2.5	149	150, 104
1,3-Dichlorobenzene	7.4	1.9	146	148, 111
1,4-Dichlorobenzene	7.8	4.4	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	--	--	152	150, 115
1,2-Dichlorobenzene	8.4	1.9	146	148, 111
3,3'-Dichlorobenzidine	32.2	16.5	252	254, 126
2,4-Dichlorophenol	9.8	2.7	162	164, 98
2,6-Dichlorophenol	--	--	162	164, 98
Dieldrin	27.2	2.5	79	263, 279
Diethylphthalate	20.1	1.9	149	177, 150
p-Dimethylaminoazobenzene	--	--	120	225, 77
7,12-Dimethylbenz(a)anthracene	--	--	256	241, 257
α-,α-Dimethylphenethylamine	--	--	58	91, 42
2,4-Dimethylphenol	9.4	2.7	122	107, 121
Dimethylphthalate	18.3	1.6	163	194, 164
4,6-Dinitro-2-methylphenol	16.2	24	198	51, 105
2,4-Dinitrophenol	15.9	42	184	63, 154
2,4-Dinitrotoluene	19.8	5.7	165	63, 89
2,6-Dinitrotoluene	18.7	1.9	165	63, 89
Diphenylamine	--	--	169	168, 167
1,2-Diphenylhydrazine	--	--	77	105, 182
Di-n-octylphthalate	32.5	2.5	149	167, 43
Endosulfan I[a]	26.4	--	195	339, 341
Endosulfan II[a]	28.6	--	337	339, 341
Endosulfan sulfate	29.8	5.6	272	387, 422
Endrin[a]	27.9	--	263	82, 81
Endrin aldehyde	--	--	67	345, 250
Endrin ketone	--	--	317	67, 319
Ethyl methanesulfonate	--	--	79	109, 97
Fluoranthene	26.5	2.2	202	101, 203
Fluorene	19.5	1.9	166	165, 167
2-Fluorobiphenyl (surr.)	--	--	172	171
2-Fluorophenol (surr.)	--	--	112	64
Heptachlor	23.4	1.9	100	272, 274
Heptachlor epoxide	25.6	2.2	353	355, 351
Hexachlorobenzene	21.0	1.9	284	142, 249
Hexachlorobutadiene	11.4	0.9	225	223, 227
Hexachlorocyclopentadiene[a]	13.9	--	237	235, 272
Hexachloroethane	8.4	1.6	117	201, 199
Indeno(1,2,3-cd)pyrene	42.7	3.7	276	138, 227

TABLE 1. - Continued

Compound	Retention Time (min)	Method detection limit (ug/L)	Primary Ion	Secondary Ion(s)
Isophorone	11.9	2.2	82	95, 138
Methoxychlor	--	--	227	228
3-Methylcholanthrene	--	--	268	253, 267
Methyl methanesulfonate	--	--	80	79, 65
2-Methylnaphthalene	--	--	142	141
2-Methylphenol	--	--	108	107, 79
4-Methylphenol	--	--	108	107, 79
Naphthalene	12.1	1.6	128	129, 127
Naphthalene-d_8 (I.S.)	--	--	136	68
1-Naphthylamine	--	--	143	115, 116
2-Naphthylamine	--	--	143	115, 116
2-Nitroaniline	--	--	65	92, 138
3-Nitroaniline	--	--	138	108, 92
4-Nitroaniline	--	--	138	108, 92
Nitrobenzene	11.1	1.9	77	123, 65
Nitrobenzene-d_5 (surr.)	--	--	82	128, 54
2-Nitrophenol	6.5	3.6	139	109, 65
4-Nitrophenol	20.3	2.4	139	109, 65
N-Nitroso-di-n-butylamine	--	--	84	57, 41
N-Nitrosodimethylamine[a]	--	--	42	74, 44
N-Nitrosodiphenylamine[a]	20.5	1.9	169	168, 167
N-Nitroso-di-N-propylamine	--	--	70	130, 42
N-Nitrosopiperidine	--	--	42	114, 55
Pentachlorobenzene	--	--	250	252, 248
Pentachloronitrobenzene	--	--	295	237, 142
Pentachlorophenol	17.5	3.6	266	264, 268
Perylene-d_{12} (I.S.)	--	--	264	260, 265
Phenacetin	--	--	108	109, 179
Phenanthrene	22.8	5.4	178	179, 176
Phenanthrene-d_{10} (I.S.)	--	--	188	94, 80
Phenol	8.0	1.5	94	65, 66
Phenol-d_6 (surr.)	--	--	99	42, 71
2-Picoline	--	--	93	66, 92
Pronamide	--	--	173	175, 145
Pyrene	27.3	1.9	202	200, 203
Terphenyl-d_{14} (surr.)	--	--	244	122, 212
1,2,4,5-Tetrachlorobenzene	--	--	216	214, 218
2,3,4,6-Tetrachlorophenol	--	--	232	230, 131
2,4,6-Tribromophenol (surr.)	--	--	330	332, 141
1,2,4-Trichlorobenzene	11.6	1.9	180	182, 145
2,4,5-Trichlorophenol	--	--	196	198, 200
2,4,6-Trichlorophenol	11.8	2.7	196	198, 200
Toxaphene[b]	25-34	--	159	231, 233

[a]See Section 1.3
[b]These compounds are mixtures of various isomers.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

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2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system:

4.1.1 **Gas chromatograph:** An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases.

4.1.2 **Columns:**

4.1.2.1 For base/neutral compound detection: 2-m x 2-mm I.D. stainless or glass, packed with 3% SP-2250-DB on 100/120 mesh Supelcoport or equivalent.

4.1.2.2 For acid compound detection: 2-m x 2-mm I.D. glass, packed with 1% SP-1240-DA on 100/120 mesh Supelcoport or equivalent.

4.1.3 **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 all of the criteria in Table 3 when 1 uL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 **GC/MS interface:** Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA [a]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

[a] J.W. Eichelberger, L.E. Harris, and W.L. Budde. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry", Analytical Chemistry, 47, 995 (1975).

used. GC-to-MS interfaces constructed entirely of glass or glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.1.5 **Data system:** A computer system must be interfaced to the mass spectrometer. The system must 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 any 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 an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

4.2 Syringe: 10-uL.

5.0 REAGENTS

5.1 Stock standard solutions (1.00 ug/uL): Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent 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.

5.1.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C 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.

5.1.3 Stock standard solutions must be replaced after 1 yr or sooner if comparison with quality control check samples indicates a problem.

5.2 Internal standard solutions: The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Paragraph 7.3.2 are met. Dissolve 200 mg of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide.

Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/ul. Each 1-mL sample extract undergoing analysis should be spiked with 10 uL of the internal standard solution, resulting in a concentration of 40 ng/uL of each internal standard. Store at 4°C or less when not being used.

5.3 GC/MS tuning standard: A methylene chloride solution containing 50 ng/uL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/uL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at 4°C or less when not being used.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). Each 1-mL aliquot of calibration standard should be spiked with 10 uL of the internal standard solution prior to analysis. All standards should be stored at -10°C to -20°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.5 Surrogate standards: The recommended surrogate standards are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.6 Matrix spike standards: See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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7.0 PROCEDURE

7.1 Sample preparation: Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

7.1.1 **Direct injection:** In very limited applications direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted where concentrations in excess of 10,000 ug/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3640, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorous pesticides	3620, 3640
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

[a]Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration: The recommended GC/MS operating conditions:

Electron energy: 70 volts (nominal)
Mass range: 35-500 amu
Scan time: 1 sec/scan
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
Sample volume: 1-2 uL
Carrier gas: Helium at 30 mL/min

Conditions for base/neutral analysis (3% SP-2250-DB):

Initial column temperature and hold time: 50°C for 4 min
Column temperature program: 50-300°C at 8°C/min
Final column temperature hold: 300°C for 20 min

Conditions for acid analysis (1% SP-1240-DA):

Initial column temperature and hold time: 70°C for 2 min
Column temperature program: 70-200°C at 8°C/min
Final column temperature hold: 200°C for 20 min

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning.

7.3.2 The internal standards selected in Paragraph 5.1 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion, i.e., for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation.

7.3.3 Analyze 1 uL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

where:

A_x = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_x = Concentration of the compound being measured (ng/uL).

C_{is} = Concentration of the specific internal standard (ng/uL).

7.3.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD = 100[SD/$\overline{RF}$]) should also be calculated for each compound. The %RSD should be less than 30% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.5 A system performance check must be performed to ensure that minimum average response factors are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol. The minimum acceptable average RF for these is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.4 Daily GC/MS calibration:

7.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12-hr shift.

7.4.2 A calibration standard(s) at mid-level concentration containing all semivolatile analytes, including all required surrogates, must be performed every 12-hr during analysis. Compare the response factor data from the standards every 12-hr with the average response factor from the initial calibration for a specific instrument as per SPCC (Paragraph 7.4.3) and CCC (Paragraph 7.4.4) criteria.

7.4.3 **System Performance Check Compounds** (SPCCs): A system performance check must be made during every 12 hr shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.4.4 **Calibration Check Compounds** (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration. Calculate the percent difference using:

TABLE 4. CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-Octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_C}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_C = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met (>30% difference) for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect these criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

7.4.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

7.5 GC/MS analysis:

7.5.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Spike the 1-mL extract obtained from sample preparation with 10 uL of the internal standard solution just prior to analysis.

7.5.3 Analyze the 1-mL extract by GC/MS using the appropriate column (as specified in Paragraph 4.1.2). The recommended GC/MS operating conditions to be used are specified in Paragraph 7.3.

7.5.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/uL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.5.5 Perform all qualitative and quantitative measurements as described in Paragraph 7.6. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Data interpretation:

7.6.1 Qualitative analysis:

7.6.1.1 An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference compounds should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.6.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hrs as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.6.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum.

7.6.1.1.3 The relative intensities of ions specified in Paragraph 7.6.1.1.2 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.6.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted (e.g., for EPA Contract Laboratory Program requirements, up to 20 substances of greatest apparent concentration not listed in the Hazardous Substance List must be tentatively identified). Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will

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the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in sample the spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.6.2 **Quantitative analysis:**

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g., see Table 5).

7.6.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water:

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitroso-di-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr.)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr.) = surrogate

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TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (Continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butylbenzylphthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	p-Dimethylaminoazobenzene	7,12-Dimethylbenz-(a)anthracene
Fluoranthene	Pyrene	Di-n-octylphthalate
Hexachlorobenzene	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd)pyrene
N-Nitrosodiphenylamine		3-Methylcholanthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

V_t = Volume of total extract, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean V_t = 10,000 uL. If half the base/neutral extract and half the acid extract are combined, V_t = 2,000.

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Paragraph 7.3.3).

V_o = Volume of water extracted (mL).

V_i = Volume of extract injected (uL).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis):

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, V_t, A_{is}, RF, V_i = same as for water.

W_s = weight of sample extracted or diluted in grams.

D = (100 - % moisture in sample)/100, or 1 for a wet-weight basis.

7.6.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.4 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

7.6.2.5 Quantitation of multicomponent compounds (e.g., Aroclors) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD by Method 8080.

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8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g, column changed), recalibration of the system must take place.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the DFTPP specifications in Section 7.3.1 and 7.4.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in 7.3.

8.4.3 The GC/MS system must meet the SPCC criteria specified in 7.4.3 and the CCC criteria in 7.4.4, each 12 hr.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality (QC) check sample concentrate is required containing each analyte at a concentration of 100 ug/mL in acetone. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the

QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Using a pipet, prepare QC check samples at a concentration of 100 ug/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.5.3 Analyze the well-mixed QC check samples according to the method beginning in Section 7.1 with extraction of the samples.

8.5.4 Calculate the average recovery ($\bar{X}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte of interest using the four results.

8.5.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all analytes of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.5.2.

8.5.6.2 Beginning with Section 8.5.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.6.1 The concentration of the spike in the sample should be determined as follows:

8.6.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or

TABLE 6. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27.133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octylphthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113

TABLE 6. QC ACCEPTANCE CRITERIA[a] - Continued

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitroso-di-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

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1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at 100 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 ug/L.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as $100(A-B)\%/T$, where T is the known true value of the spike.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Section 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.96C+0.19	0.15X-0.12	0.21X-0.67
Acenaphthylene	0.89C+0.74	0.24X-1.06	0.26X-0.54
Aldrin	0.78C+1.66	0.27X-1.28	0.43X+1.13
Anthracene	0.80C+0.68	0.21X-0.32	0.27X-0.64
Benzo(a)anthracene	0.88C-0.60	0.15X+0.93	0.26X-0.21
Chloroethane	0.99C-1.53	0.14X-0.13	0.17X-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22X+0.43	0.29X+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19X+1.03	0.35X+0.40
Benzo(a)pyrene	0.90C-0.13	0.22X+0.48	0.32X+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29X+2.40	0.51X-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18X+0.94	0.53X+0.92
β-BHC	0.87C-0.94	0.20X-0.58	0.30X+1.94
δ-BHC	0.29C-1.09	0.34X+0.86	0.93X-0.17
Bis(2-chloroethyl)ether	0.86C-1.54	0.35X-0.99	0.35X+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16X+1.34	0.26X+2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24X+0.28	0.25X+1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26X+0.73	0.36X+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13X+0.66	0.16X+0.66
2-Chloronaphthalene	0.89C+0.01	0.07X+0.52	0.13X+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20X-0.94	0.30X-0.46
Chrysene	0.93C-1.00	0.28X+0.13	0.33X-0.09
4,4'-DDD	0.56C-0.40	0.29X-0.32	0.66X-0.96
4,4'-DDE	0.70C-0.54	0.26X-1.17	0.39X-1.04
4,4'-DDT	0.79C-3.28	0.42X+0.19	0.65X-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30X+8.51	0.59X+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13X+1.16	0.39X+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20X+0.47	0.24X+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25X+0.68	0.41X+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24X+0.23	0.29X+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28X+7.33	0.47X+3.45
Dieldrin	0.82C-0.16	0.20X-0.16	0.26X-0.07
Diethyl phthalate	0.43C+1.00	0.28X+1.44	0.52X+0.22
Dimethyl phthalate	0.20C+1.03	0.54X+0.19	1.05X-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12X+1.06	0.21X+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14X+1.26	0.19X+0.35
Di-n-octylphthalate	0.76C-0.79	0.21X+1.19	0.37X+1.19
Endosulfan sulfate	0.39C+0.41	0.12X+2.47	0.63X-1.03
Endrin aldehyde	0.76C-3.86	0.18X+3.91	0.73X-0.62
Fluoranthene	0.81C+1.10	0.22X-0.73	0.28X-0.60
Fluorene	0.90C-0.00	0.12X+0.26	0.13X+0.61
Heptachlor	0.87C-2.97	0.24X-0.56	0.50X-0.23
Heptachlor epoxide	0.92C-1.87	0.33X-0.46	0.28X+0.64
Hexachlorobenzene	0.74C+0.66	0.18X-0.10	0.43X-0.52
Hexachlorobutadiene	0.71C-1.01	0.19X+0.92	0.26X+0.49
Hexachloroethane	0.73C-0.83	0.17X+0.67	0.17X+0.80

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a] - Continued

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{X}$+1.46	0.50$\bar{X}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{X}$+0.77	0.33$\bar{X}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{X}$-0.41	0.30$\bar{X}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{X}$+0.92	0.27$\bar{X}$+0.21
N-Nitroso-di-n-propylamine	1.12C-6.22	0.27$\bar{X}$+0.68	0.44$\bar{X}$+0.47
PCB-1260	0.81C-10.86	0.35$\bar{X}$+3.61	0.43$\bar{X}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{X}$+0.57	0.15$\bar{X}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{X}$+0.06	0.15$\bar{X}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{X}$+0.85	0.21$\bar{X}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{X}$+0.75	0.29$\bar{X}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{X}$+1.46	0.28$\bar{X}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{X}$+1.25	0.21$\bar{X}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{X}$+1.21	0.22$\bar{X}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{X}$+2.36	0.42$\bar{X}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{X}$+42.29	0.26$\bar{X}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{X}$+1.94	0.27$\bar{X}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{X}$+2.57	0.44$\bar{X}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{X}$+3.03	0.30$\bar{X}$+4.33
Phenol	0.43C+1.26	0.26$\bar{X}$+0.73	0.35$\bar{X}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{X}$+2.22	0.22$\bar{X}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

If the entire list of analytes in Table 6 must be measured in the sample in Section 8.6, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.7.1 Prepare the QC check standard by adding 1.0 mL of the QC check sample concentrate (Section 8.5.1 or 8.6.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyzed the QC check standard to determine the concentration measured (A) of each analyte. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.7.3 Compare the percent recovery (P_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix) as in Section 8.6, calculate the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p}$ = 90% and s_p = 10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 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. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or mass spectrometry using other ionization modes must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method 8250 was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 ug/L. Single operator accuracy and precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Method 625," October 26, 1984.

TABLE 8. SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

3. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63, 1983.

4. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

5. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

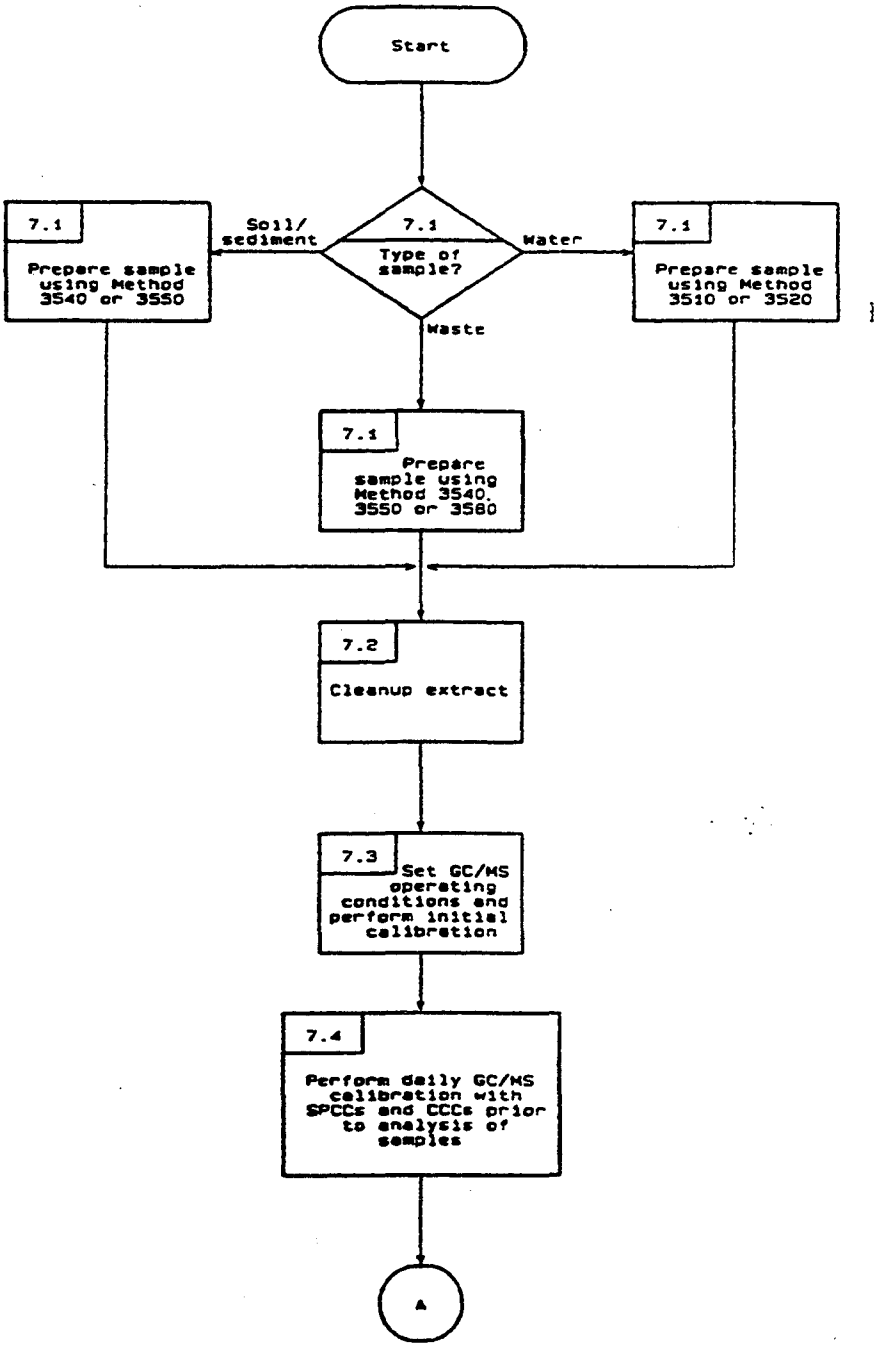
6. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).

7. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

METHOD 8250

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS:

PACKED COLUMN TECHNIQUE



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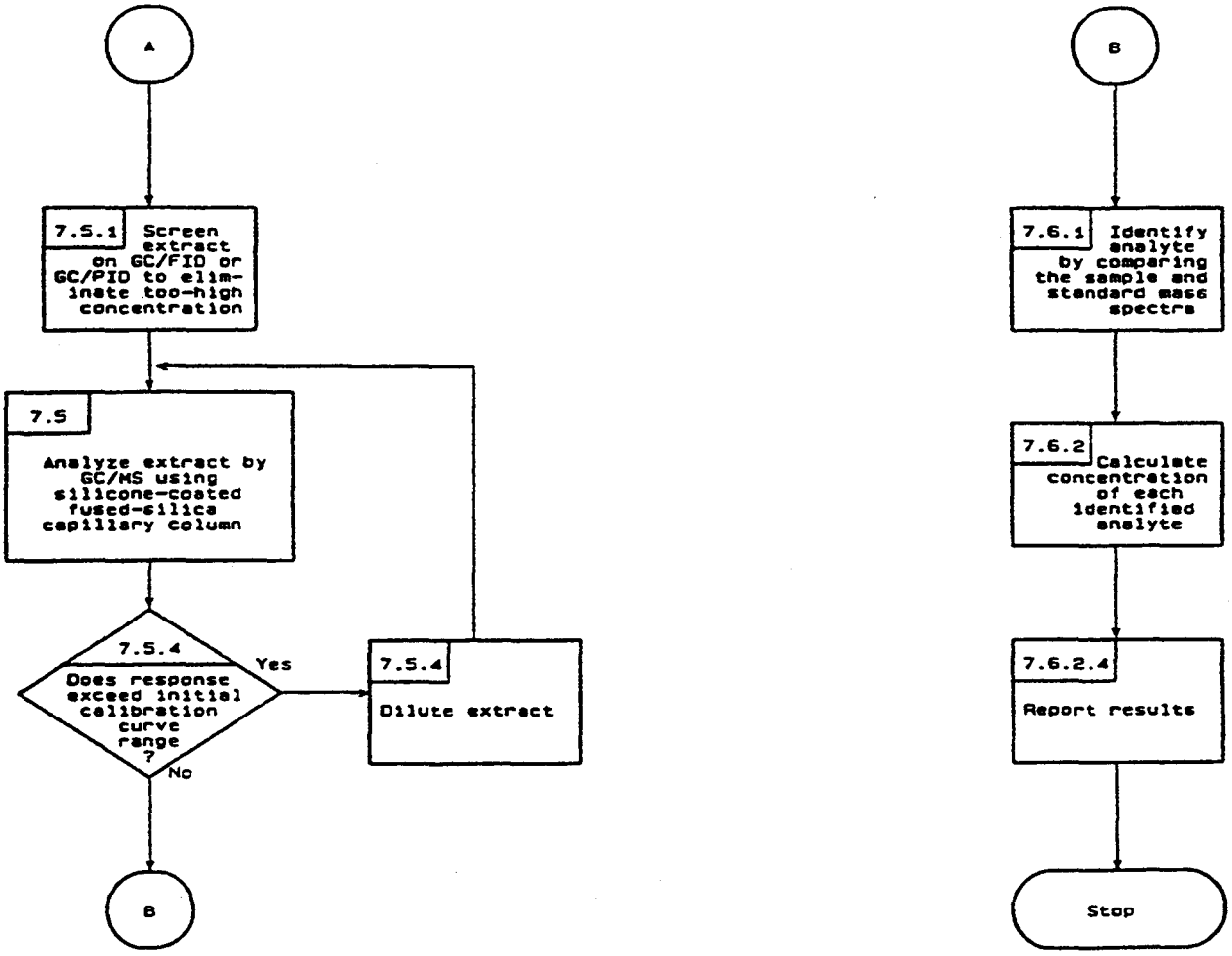
A
7.5.1 Screen extract on GC/FID or GC/PID to eliminate too-high concentration
7.5 Analyze extract by GC/MS using silicone-coated fused-silica capillary column
7.5.4 Does response exceed initial calibration curve range ?
Yes
No
7.5.4 Dilute extract
B
B
7.6.1 Identify analyte by comparing the sample and standard mass spectra
7.6.2 Calculate concentration of each identified analyte
7.6.2.4 Report results
Stop