

A Fast Method for EPA 8270 in MRM Mode Using the 7000 Series Triple Quadrupole GC/MS

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Introduction

A fast method for EPA 8270D/E has been developed for the Agilent 7000 series triple quadrupole GC/MS system in multiple reaction monitoring (MRM) mode. In addition to increased sensitivity, the high selectivity afforded by MRM results in faster batch review due to the elimination of matrix interferences that might be present when using SIM or extraction ions in scan mode. This method meets performance requirements for calibration over a working range of 0.02 to 160 ppm in a single 10 minute run. Low initial calibration compound %RSDs are predictive of an extended continuing calibration, which reduces the cost of operation. The methodology described here for the analysis of semivolatile organic compounds by GC/MS is applicable to the United States EPA Method 8270D/E as well as to other regions worldwide.

Experimental

A 7000C or D triple quadrupole mass spectrometer was coupled to an Agilent 8890 or 7890B GC with a 240 V oven for fast temperature programming. The GC was equipped with an SSL inlet, and the system was autotuned using the etune algorithm. The analytical method used an Agilent low-pressure-drop (LPD) GC inlet liner (p/n 5190-2295) and an Agilent J&W DB-5ms Ultra Inert column, 20 m × 0.18, 0.18 μm (p/n 121-5522UI). A 1 μL injection was made in split mode using a 1:20 split ratio, which was optimized as described under Split Ratio and Detector Gain Optimization. The ion source was equipped with a 9 mm diameter drawout lens (p/n G3870-20449). A total of 12 or 13 calibration levels ranging from 0.02 to 160 ppm were prepared in dichloromethane using a 77-compound mix and six internal standards (ISTDs) (AccuStandard). ISTD concentration was at the midpoint (4 ppm), and the method was retention time locked to acenaphthene-d₁₀. Agilent MassHunter Workstation Quantitative Analysis software was used for data acquisition and processing. MRM data were collected in dynamic MRM (dMRM) mode for efficient use of instrument analytical time. Tables 1 and 2 contain detailed method parameters and MRM transitions, respectively.

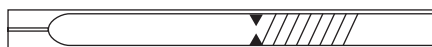


Figure 1. LPD GC inlet liner with glass wool (p/n 5190-2295).

Table 1. Agilent 8890/7890 GC and Agilent 7000 C/D instrument conditions.

GC Conditions	
Analytical Column	Agilent J&W DB-5ms Ultra Inert, 20 m × 0.18, 0.18 μm (p/n 121-5522UI)
Injection Volume	1 μL
Inlet Temperature	Isothermal at 280 °C
Injection Mode	Split ratio 1:20
Oven Temperature	40 °C, hold for 0 minute 40 °C to 320 °C at 35 °C/min, hold for 2 minutes
Carrier Gas	Helium, constant flow at 1.2 mL/min
Transfer Line Temperature	320 °C
Run Time	10 minutes
MS Conditions	
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Ionization	EI mode
EMV Mode	Gain factor
Gain Factor	2 (optimized for each system)
Solvent Delay	1.25 minutes
Scan Type	dMRM
Cycles Per Second	6.6

Table 2. MRM transitions (dMRM acquisition mode). Optimized delta retention time (RT) and dwell time values were truncated for the sake of clarity.

Compound	RT	Precursor Ion	Product Ion	Left RT delta	Right RT delta	Dwell	CE
NDMA	1.38	74	44	0.13	0.20	56.07	6
NDMA	1.38	74	42	0.13	0.20	56.07	14
Pyridine	1.41	79	52	0.10	0.20	56.07	25
Pyridine	1.41	79	51	0.10	0.20	56.07	25
Phenol, 2-fluoro-	1.91	112	64	0.10	0.12	75.06	20
Phenol, 2-fluoro-	1.91	112	63	0.10	0.12	75.06	45
Phenol-d ₆	2.34	99	71	0.10	0.15	14.17	30
Phenol-d ₆	2.34	99	42	0.10	0.15	14.17	40
Phenol	2.35	94	66.1	0.10	0.15	14.17	15
Phenol	2.35	94	65.1	0.10	0.15	14.17	20
Aniline	2.38	93	66	0.10	0.15	10.50	10
Aniline	2.38	92	65	0.10	0.15	10.50	10
bis(2-Chloroethyl)ether	2.41	95.1	65	0.10	0.10	9.53	5
bis(2-Chloroethyl)ether	2.41	93.1	63	0.10	0.10	9.53	0
Chlorophenol, 2-	2.45	128	64	0.10	0.15	9.22	15
Chlorophenol, 2-	2.45	128	63	0.10	0.15	9.22	30
1,3-Dichlorobenzene	2.54	146	111	0.20	0.42	8.33	15
1,3-Dichlorobenzene	2.54	146	75	0.20	0.42	8.33	30
1,4-Dichlorobenzene-d ₄	2.57	150	115	0.10	0.10	9.31	15
1,4-Dichlorobenzene-d ₄	2.57	150	78	0.10	0.10	9.31	30

Table 2. MRM transitions (dMRM acquisition mode). Optimized delta RT and dwell time values were truncated for the sake of clarity (continued).

Compound	RT	Precursor Ion	Product Ion	Left RT delta	Right RT delta	Dwell	CE
1,4-Dichlorobenzene	2.58	146	111	0.42	0.42	13.21	15
1,4-Dichlorobenzene	2.58	146	75	0.42	0.42	13.21	30
Benzyl alcohol	2.64	108	79	0.10	0.20	8.84	15
Benzyl alcohol	2.64	107	79	0.10	0.20	8.84	5
1,2-Dichlorobenzene	2.67	146	111	0.42	0.20	9.63	15
1,2-Dichlorobenzene	2.67	146	75	0.42	0.20	9.63	30
Methylphenol, 2- (Cresol, o-)	2.7	108	107	0.15	0.20	7.96	15
Methylphenol, 2- (Cresol, o-)	2.7	107	77	0.15	0.20	7.96	15
bis(2-Chloro-1-methylethyl)ether	2.73	121	77	0.15	0.25	7.68	5
bis(2-Chloro-1-methylethyl)ether	2.73	121	49	0.15	0.25	7.68	30
Methylphenol, 4- (Cresol, p-)	2.8	108	107.1	0.20	0.25	8.36	15
Methylphenol, 4- (Cresol, p-)	2.8	107	77.1	0.20	0.25	8.36	15
Nitrosodi-n-propylamine, N-	2.81	113.1	71	0.10	0.15	7.14	10
Nitrosodi-n-propylamine, N-	2.81	101	70	0.10	0.15	7.14	0
Hexachloroethane	2.88	200.9	165.9	0.10	0.12	7.19	15
Hexachloroethane	2.88	118.9	83.9	0.10	0.12	7.19	35
Nitrobenzene-D ₅	2.91	128	98	0.10	0.10	7.78	10
Nitrobenzene-D ₅	2.91	128	82	0.10	0.10	7.78	10
Nitrobenzene	2.92	123	77	0.10	0.15	8.28	10
Nitrobenzene	2.92	77	51	0.10	0.15	8.28	15
Isophorone	3.07	138	82	0.20	0.25	10.46	5
Isophorone	3.07	82	54	0.20	0.25	10.46	5
Nitrophenol, 2-	3.12	138.9	81	0.15	0.22	11.00	15
Nitrophenol, 2-	3.12	109	81	0.15	0.22	11.00	10
Dimethylphenol, 2,4- (2,4-xylenol)	3.14	122.1	107	0.10	0.15	12.24	10
Dimethylphenol, 2,4- (2,4-xylenol)	3.14	107.1	77.1	0.10	0.15	12.24	15
Benzoic acid	3.18	105	77	0.20	0.35	11.42	10
Benzoic acid	3.18	105	51	0.20	0.35	11.42	35
bis(2-Chloroethoxy)methane	3.21	95	65	0.10	0.15	10.37	5
bis(2-Chloroethoxy)methane	3.21	93	63	0.10	0.15	10.37	5
Dichlorophenol, 2,4-	3.28	163.9	63	0.10	0.15	9.65	30
Dichlorophenol, 2,4-	3.28	162	63	0.10	0.15	9.65	30
Trichlorobenzene, 1,2,4-	3.34	179.9	145	0.10	0.15	10.32	15
Trichlorobenzene, 1,2,4-	3.34	179.9	109	0.10	0.15	10.32	30
Naphthalene-d ₈	3.38	136.1	108.1	0.10	0.10	9.59	20
Naphthalene-d ₈	3.38	136.1	84.1	0.10	0.10	9.59	25
Naphthalene	3.39	128.1	102.1	0.10	0.15	12.38	20
Naphthalene	3.39	128.1	78.1	0.10	0.15	12.38	20
Chloroaniline, 4-	3.42	127	92	0.10	0.15	13.18	15
Chloroaniline, 4-	3.42	127	65	0.10	0.15	13.18	20
Hexachlorobutadiene	3.47	226.9	191.9	0.10	0.15	28.71	15
Hexachlorobutadiene	3.47	224.8	189.9	0.10	0.15	28.71	15

Table 2. MRM transitions (dMRM acquisition mode). Optimized delta RT and dwell time values were truncated for the sake of clarity (continued).

Compound	RT	Precursor Ion	Product Ion	Left RT delta	Right RT delta	Dwell	CE
Phenol, 4-chloro-3-methyl-	3.75	142	107	0.15	0.25	34.24	15
Phenol, 4-chloro-3-methyl-	3.75	107	77	0.15	0.25	34.24	15
Methylnaphthalene, 2-	3.86	142.1	141.1	0.10	0.15	22.34	15
Methylnaphthalene, 2-	3.86	141.1	115.1	0.10	0.15	22.34	15
Hexachlorocyclopentadiene	3.97	237	143	0.10	0.15	17.85	20
Hexachlorocyclopentadiene	3.97	237	119	0.10	0.15	17.85	20
Trichlorophenol, 2,4,5-	4.05	197.9	97	0.10	0.20	16.66	25
Trichlorophenol, 2,4,5-	4.05	195.9	97	0.10	0.20	16.66	25
Trichlorophenol, 2,4,6-	4.07	198	97	0.10	0.20	17.45	30
Trichlorophenol, 2,4,6-	4.07	196	97	0.10	0.20	17.45	30
1,1'-Biphenyl, 2-fluoro-	4.11	172	171	0.10	0.10	16.20	35
1,1'-Biphenyl, 2-fluoro-	4.11	172	170	0.10	0.10	16.20	35
Chloronaphthalene, 2-	4.2	162	127.1	0.10	0.10	21.04	20
Chloronaphthalene, 2-	4.2	162	77	0.10	0.10	21.04	35
Nitroaniline, 2-	4.27	138	92	0.10	0.10	25.89	15
Nitroaniline, 2-	4.27	138	65	0.10	0.10	25.89	25
Dimethyl phthalate	4.4	163	92	0.10	0.10	23.89	30
Dimethyl phthalate	4.4	163	77	0.10	0.10	23.89	20
Dinitrotoluene, 2,6-	4.44	165	90.1	0.10	0.10	20.02	15
Dinitrotoluene, 2,6-	4.44	165	63	0.10	0.10	20.02	25
Acenaphthylene	4.49	152.1	102.1	0.10	0.15	14.15	30
Acenaphthylene	4.49	151.1	77	0.10	0.15	14.15	25
Nitroaniline, 3-	4.55	138	92	0.10	0.15	11.18	15
Nitroaniline, 3-	4.55	138	80	0.10	0.15	11.18	5
Acenaphthene-d ₁₀	4.59	164.1	162.1	0.10	0.10	10.43	15
Acenaphthene-d ₁₀	4.59	162.1	160.1	0.10	0.10	10.43	20
Acenaphthene	4.61	154.1	127	0.10	0.10	10.43	40
Acenaphthene	4.61	153.1	77	0.10	0.10	10.43	45
Phenol, 2,4-dinitro-	4.63	184	107	0.20	0.60	12.76	25
Phenol, 2,4-dinitro-	4.63	184	79	0.20	0.60	12.76	25
Nitrophenol, 4-	4.67	138.9	109	0.15	0.24	12.71	5
Nitrophenol, 4-	4.67	109	81	0.15	0.24	12.71	10
Dinitrotoluene, 2,4-	4.72	165	119	0.10	0.10	12.55	5
Dinitrotoluene, 2,4-	4.72	165	63	0.10	0.10	12.55	45
Dibenzofuran	4.73	168.1	139.1	0.10	0.10	13.47	25
Dibenzofuran	4.73	139.1	63	0.10	0.10	13.47	35
Diethyl phthalate	4.89	149	93	0.10	0.10	12.42	15
Diethyl phthalate	4.89	149	65	0.10	0.10	12.42	20
Fluorene	4.97	166.1	165.1	0.10	0.12	10.14	15
Fluorene	4.97	165.1	163.1	0.10	0.12	10.14	35
Nitroaniline, 4-	4.98	138	108.1	0.10	0.15	10.10	5

Table 2. MRM transitions (dMRM acquisition mode). Optimized delta RT and dwell time values were truncated for the sake of clarity (continued).

Compound	RT	Precursor Ion	Product Ion	Left RT delta	Right RT delta	Dwell	CE
Nitroaniline, 4-	4.98	108	80	0.10	0.15	10.10	15
Chlorophenyl phenyl ether, 4-	4.98	204	77	0.10	0.15	10.34	30
Chlorophenyl phenyl ether, 4-	4.98	141.1	115.1	0.10	0.15	10.34	20
DNOC (2-methyl-4,6-dinitrophenol)	5	198	167.9	0.10	0.25	13.44	5
DNOC (2-methyl-4,6-dinitrophenol)	5	198	121	0.10	0.25	13.44	10
Nitrosodiphenylamine, N-	5.06	169.1	168.1	0.10	0.12	9.76	15
Nitrosodiphenylamine, N-	5.06	168.1	167.1	0.10	0.12	9.76	15
Azobenzene	5.09	105	77.1	0.11	0.12	11.37	5
Azobenzene	5.09	77	51	0.11	0.12	11.37	15
Tribromophenol, 2,4,6-	5.14	329.7	140.8	0.10	0.12	16.41	30
Tribromophenol, 2,4,6-	5.14	140.9	62	0.10	0.12	16.41	15
4-Bromophenyl phenyl ether	5.32	250	141	0.10	0.10	22.75	20
4-Bromophenyl phenyl ether	5.32	248	141	0.10	0.10	22.75	20
Hexachlorobenzene	5.36	283.8	213.9	0.10	0.10	28.52	30
Hexachlorobenzene	5.36	248.9	214	0.10	0.10	28.52	15
Pentachlorophenol	5.5	265.9	167	0.10	0.42	30.92	25
Pentachlorophenol	5.5	165	130	0.10	0.42	30.92	25
Phenanthrene	5.62	178.1	152.1	0.12	0.16	22.36	25
Phenanthrene	5.62	176.1	150.1	0.12	0.16	22.36	25
Phenanthrene-d ₁₀	5.64	188.3	160.2	0.10	0.10	18.93	20
Phenanthrene-d ₁₀	5.64	188.3	158.2	0.10	0.10	18.93	35
Anthracene	5.69	178.1	152.1	0.12	0.14	18.72	25
Anthracene	5.69	178.1	151.1	0.12	0.14	18.72	30
Carbazole	5.81	167	139	0.10	0.12	33.75	45
Carbazole	5.81	167	89	0.10	0.12	33.75	60
Di- <i>n</i> -butyl phthalate	6.06	149	121	0.10	0.10	74.98	15
Di- <i>n</i> -butyl phthalate	6.06	149	65	0.10	0.10	74.98	25
Fluoranthene	6.5	202.1	152.1	0.10	0.22	26.52	30
Fluoranthene	6.5	201.1	200.1	0.10	0.22	26.52	15
Benzidine	6.6	184	156	0.10	0.25	25.99	45
Benzidine	6.6	184	139	0.10	0.25	25.99	55
Pyrene	6.66	202.1	151	0.10	0.15	21.27	45
Pyrene	6.66	201.1	200	0.10	0.15	21.27	15
<i>p</i> -Terphenyl-d ₁₄	6.76	244	240	0.38	0.38	36.14	45
<i>p</i> -Terphenyl-d ₁₄	6.76	244	226	0.38	0.38	36.14	40
Butyl benzyl phthalate	7.14	149	65	0.10	0.10	55.86	25
Butyl benzyl phthalate	7.14	91	65	0.10	0.10	55.86	15
3,3'-Dichlorobenzidine	7.5	252	181	0.10	0.12	25.65	45
3,3'-Dichlorobenzidine	7.5	252	154	0.10	0.12	25.65	55
Benz[a]anthracene	7.51	228.1	226.1	0.10	0.15	23.12	30
Benz[a]anthracene	7.51	226.1	224.1	0.10	0.15	23.12	35
Chrysene-d ₁₂	7.52	240.2	236.2	0.08	0.12	16.17	35

Sample split ratio and detector gain optimization

Optimizing the amount of sample introduced and the detector gain leads to the widest dynamic range. Using the highest-level calibration standard (160 ppm) and a low gain setting such as 1 to avoid detector saturation, the split ratio was adjusted to meet benzo[b and k]fluoranthene isomer resolution requirements and avoid wide peaks with rounded tops. Sufficient resolution is achieved if the height of the valley between two isomer peaks is less than 50 % of the average of the two peak heights at the midpoint concentration level (EPA 8270D/E). Peak distortion patterns such as broadening (symmetrical) and rounded tops are indications of system overloading. The optimized split ratio was generally 1:20. The detector gain was then optimized for maximum linearity, which was critical to the analysis. The gain was set for the triple quadrupole instrument such that the tallest peak in the base peak chromatogram (BPC) for the highest-level calibration standard was in the range of 3 to 5 × 10⁷ counts. The gain setting for analysis was usually set to a value of 1 to 2.

The Agilent inert extractor ion source provides excellent flexibility to allow users to obtain the best possible performance to meet their method needs. For fast 8270 MRM analysis, a 9 mm diameter lens was used due to the enhanced sensitivity observed for the most challenging compounds coupled with low average RF %RSDs¹.

Calibration results

The chromatogram in Figure 2 shows the separation of 77 target compounds and six internal standards.

Passing criteria

A multipoint calibration was performed, and the relative response factor (RF) was determined for each component at each calibration level. The mean response factor was then calculated across the average relative RFs for the calibration curve of each compound, along with its relative standard deviation (RSD). Passing criteria are that the average RF %RSD must be ≤ 20 (preferred as default passing criteria); if not, $R^2 \geq 0.990$ is required for a linear curve fit; finally, a quadratic fit may be used. Accuracy for the lowest data point must be $\pm 30\%$, and six points are needed when a curve fit is used.

Table 2. MRM transitions (dMRM acquisition mode). Optimized delta RT and dwell time values were truncated for the sake of clarity (continued).

Compound	RT	Precursor Ion	Product Ion	Left RT delta	Right RT delta	Dwell	CE
Chrysene-d ₁₂	7.52	236.1	232.1	0.08	0.12	16.17	40
Chrysene	7.54	226.1	224.1	0.10	1.13	23.59	40
Chrysene	7.54	113.1	112.1	0.10	1.13	23.59	10
bis(2-Ethylhexyl) phthalate	7.55	167	149	0.10	0.12	23.09	5
bis(2-Ethylhexyl) phthalate	7.55	149	65	0.10	0.12	23.09	25
Di-n-octyl phthalate	7.98	149	93	0.10	0.20	27.51	20
Di-n-octyl phthalate	7.98	149	65	0.10	0.20	27.51	25
Benzo[b]fluoranthene	8.23	252.1	250.1	0.10	0.17	18.69	35
Benzo[b]fluoranthene	8.23	126	113.1	0.10	0.17	18.69	10
Benzo[k]fluoranthene	8.25	252.1	250.1	0.12	0.16	18.56	30
Benzo[k]fluoranthene	8.25	126.1	113.1	0.12	0.16	18.56	10
Benzo[a]pyrene	8.46	252.1	250.1	0.10	0.17	21.83	35
Benzo[a]pyrene	8.46	125	124.1	0.10	0.17	21.83	10
Perylene-d ₁₂	8.5	264.2	260.1	0.12	0.12	16.16	35
Perylene-d ₁₂	8.5	260.1	256.1	0.12	0.12	16.16	40
Indeno[1,2,3-cd]pyrene	9.36	276.1	274.1	0.10	0.40	30.66	40
Indeno[1,2,3-cd]pyrene	9.36	137	136	0.10	0.40	30.66	15
Dibenz[a,h]anthracene	9.38	278.1	276.1	0.12	0.30	24.37	35
Dibenz[a,h]anthracene	9.38	276.1	274.1	0.12	0.30	24.37	35
Benzo[g,h,i]perylene	9.6	276.1	274.1	0.35	0.40	45.33	45
Benzo[g,h,i]perylene	9.6	138	137	0.35	0.40	45.33	15

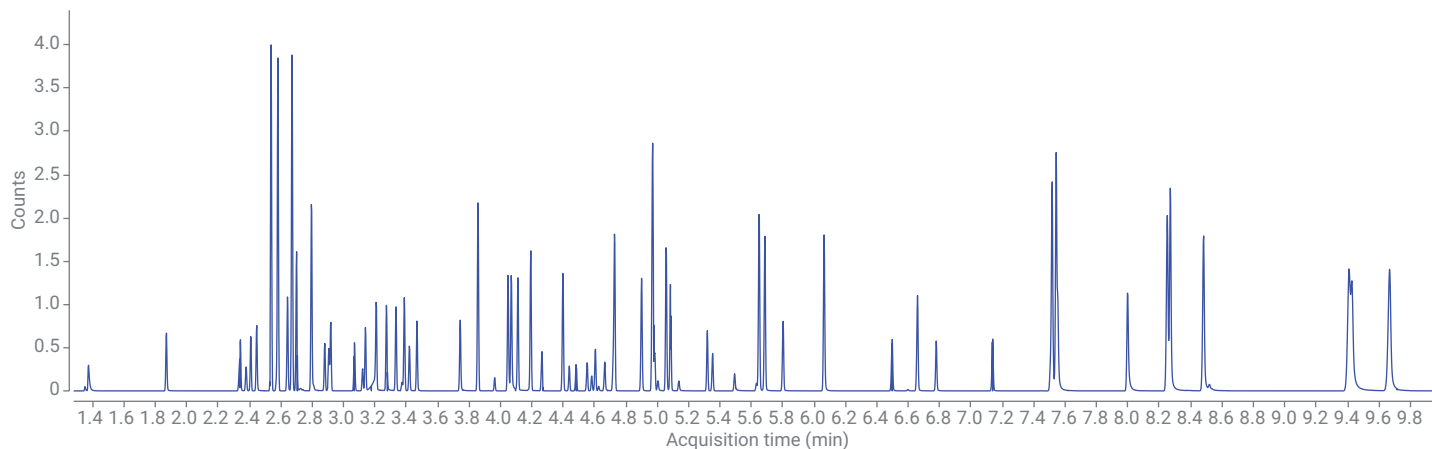


Figure 2. TIC MRM chromatogram for the 50 ppm calibration standard showing a 10 minute run time.

Initial calibration performance

Calibration results obtained from several instruments (7000C and D models) on different days were evaluated for acceptability. Results for an example initial calibration run on a 7000D system are shown in Table 3 and summarized in Table 4. The overall working range of the method was determined to be 0.02 to 160 ppm, where 0.02 ppm is 10 times lower than is commonly used for calibration. When necessary, data points for each compound at the low and high ends of the calibration range were deleted to meet method criteria, and these compounds have narrower working ranges (Table 3). Benzidine sometimes passed criteria over a broad range (for example, acceptable over 1 to 100 ppm, $R^2 = 0.9915$, linear curve fit); however, it is omitted from Table 3 since criteria were not met within this example batch. Six internal standards (dark blue), compounds that pass average RF %RSD criteria (grey), and those passing based on curve fit criteria (green) are highlighted in the table. The values for the high and low standards are 0.02 and 160 ppm, respectively, unless otherwise indicated.

Table 3. Initial calibration results for 77 target compounds.

Compound	Avg. RF %RSD	R ²	Curve Fit	Low Std (ppm)	High Std (ppm)
				(Default is 0.02 to 160 ppm)	
NDMA	30.60	0.9990	Linear	0.2	100
Pyridine	14.87	0.9887			
2-Fluorophenol	7.59	0.9950			
Phenol-d ₆	4.92	0.9988			
Phenol	7.62	0.9976			
Aniline	12.70	0.9967			100
bis(2-Chloroethyl) ether	6.19	0.9985			
2-Chlorophenol	6.71	0.9982			
1,3-Dichlorobenzene	7.84	0.9950			
1,4-Dichlorobenzene-d ₄	12.13				
1,4-Dichlorobenzene	8.30	0.9964			
Benzyl alcohol	7.52	0.9987			
1,2-Dichlorobenzene	8.02	0.9962			
2-Methylphenol (o-cresol)	8.14	0.9972			
bis(2-Chloro-1-methylethyl) ether	18.78	0.9982			
4-Methylphenol (p-cresol)	8.35	0.9986			
N-Nitrosodi-n-propylamine	12.27	0.9989			
Hexachloroethane	4.79	0.9992			
Nitrobenzene-d ₅	6.82	0.9991			
Nitrobenzene	6.03	0.9963			
Isophorone	6.49	0.9981			
2-Nitrophenol	14.75	0.9926			
2,4-Dimethylphenol (2,4-xyleneol)	13.57	0.9985			
Benzoic acid	45.77	0.9987	Quadratic	2	100
bis(2-Chloroethoxy)methane	7.07	0.9968			
2,4-Dichlorophenol	9.73	0.9984			
1,2,4-Trichlorobenzene	6.99	0.9964			
Naphthalene-d ₈	13.74				
Naphthalene	8.27	0.9956			
4-Chloroaniline	6.30	0.9971			
Hexachlorobutadiene	5.95	0.9974			
4-Chloro-3-methylphenol	8.26	0.9982			
2-Methylnaphthalene	9.95	0.9934			
Hexachlorocyclopentadiene	10.60	0.9946			
2,4,5-Trichlorophenol	12.42	0.9951			
2,4,6-Trichlorophenol	14.82	0.9967			
2-Fluorobiphenyl	8.65	0.9935			
Chloronaphthalene, 2-	7.01	0.9959			
2-Nitroaniline	12.98	0.9954			
Dimethyl phthalate	6.27	0.9979			
2,6-Dinitrotoluene	18.45	0.9945			
Acenaphthylene	5.41	0.9983			

Since several initial calibrations were run on multiple instruments, Table 4 shows a summary of results from an example batch. The presented results take a conservative approach in terms of method performance. In this example, the number of compounds that passed average RF %RSD criteria was 68 out of 77, a linear fit was used for three compounds, and five required a quadratic fit. Among the initial calibrations performed, there were instances in which no quadratic fits were required; in one case, 68 compounds passed average RF %RSD, nine passed with a linear curve fit, and the average of the internal standard average RF %RSD values was 5.7. Benzidine sometimes required a quadratic fit and did not always pass the criteria, as was the case for the batch shown. Compounds that are determined to have narrower analysis ranges during initial calibration are generally those that are known to be the most challenging in terms of GC technology, such as benzoic acid and benzidine. However, these two compounds usually passed EPA 8270 criteria using this method.

Table 3. Initial calibration results for 77 target compounds.

Compound	Avg. RF %RSD	R ²	Curve fit	Low Std (ppm)	High Std (ppm)
				(default is 0.02 to 160 ppm)	
3-Nitroaniline	17.22	0.9952			
Acenaphthene-d ₁₀	13.33				
Acenaphthene	5.81	0.9958			
2,4-Dinitrophenol	29.35	0.9959	Linear	0.5	160
4-Nitrophenol	24.22	0.9951	Linear	5	160
2,4-Dinitrotoluene	19.95	0.9973		2	160
Dibenzofuran	8.42	0.9921			
Diethyl phthalate	17.41	0.9983		0.05	160
Fluorene	7.21	0.9903			
4-Chlorophenyl phenyl ether	13.27	0.9716			
4-Nitroaniline	19.41	0.9969			
DNOC (2-Methyl-4,6-dinitrophenol)	36.98	0.9993	Quadratic	0.5	100
N-Nitrosodiphenylamine	6.23	0.9988			
Azobenzene	5.99	0.9953			
2,4,6-Tribromophenol	19.86	0.9835		0.05	100
4-Bromophenyl phenyl ether	5.59	0.9989			
Hexachlorobenzene	5.01	0.9983			
Pentachlorophenol	33.45	0.9979	Quadratic	0.5	100
Phenanthrene-d ₁₀	13.45				
Phenanthrene	5.99	0.9958			
Anthracene	5.65	0.9980			
Carbazole	6.69	0.9971			
Dibutyl phthalate	16.81	0.9962		0.05	160
Fluoranthene	8.30	0.9974			
Pyrene	8.15	0.9936			
p-Terphenyl-d ₁₄	7.30	0.9909			
Benzyl butyl phthalate	19.04	0.9815			100
3,3'-Dichlorobenzidine	15.63	0.9918			
Benzo[a]anthracene	14.30	0.9969			
Chrysene-d ₁₂	13.19				
Chrysene	5.79	0.9968			
bis(2-Ethylhexyl) phthalate	24.34	0.9978	Quadratic	0.5	100
Di-n-octyl phthalate	28.38	0.9973	Quadratic	0.5	100
Benzo[b]fluoranthene	9.72	0.9973			
Benzo[k]fluoranthene	9.69	0.9973			
Benzo[a]pyrene	11.30	0.9977			
Perylene-d ₁₂	14.94				
Indeno[1,2,3-cd]pyrene	12.64	0.9982			
Dibenz[a,h]anthracene	15.44	0.9967			
Benzo[g,h,i]perylene	8.76	0.9987			

Due to the high sensitivity achieved in MRM mode and significantly extended calibration range of 0.02 to 160 ppm, five calibration standards of concentrations less than 1 ppm were included in the batch for complete coverage. The internal standard was added at the approximate calibration standard median level of 4 ppm since it was determined that the method performed optimally when this was the case.

Table 4. Initial calibration results summary.

Number of Compounds with Average RF %RSD <20	Target Compounds Average RF %RSD (Average Over Batch)	Practical Working Range (ppm)	Internal Standard Average RF %RSD (Average for Six Compounds)
68/77	12.3	0.02 to 160	13.5

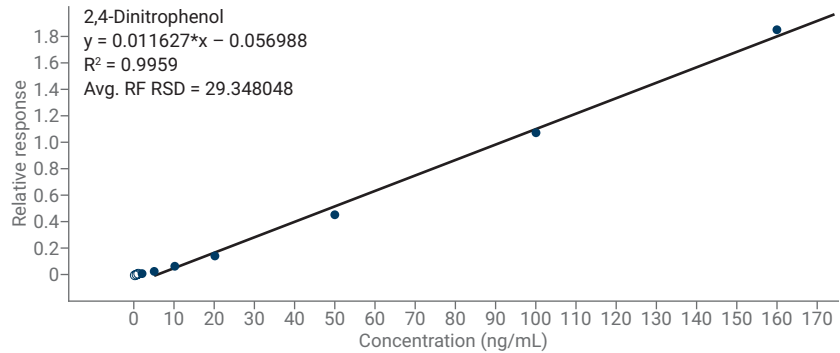


Figure 3. Example calibration results for the challenging compound 2,4-dinitrophenol. The acceptable analysis range is 2 to 160 ppm ($R^2 = 0.9959$; linear fit). Deselected points are those that are <2 ppm and were deleted to pass criteria.

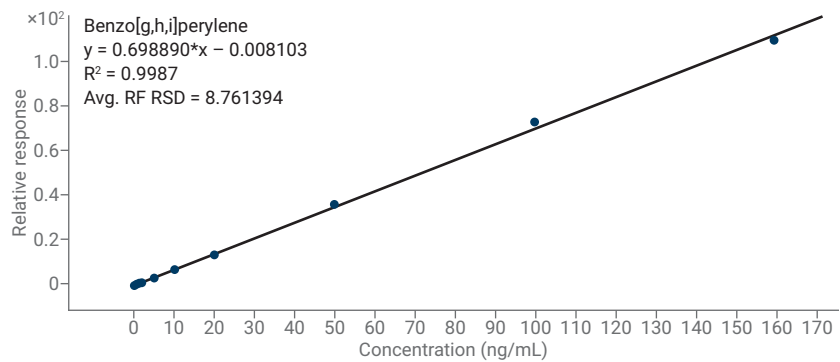


Figure 4. Example calibration results for benzo [g,h,i] perylene. The acceptable analysis range is 0.05 to 160 ppm (Avg RF %RSD = 8.8 (passes); $R^2 = 0.9987$; linear fit).

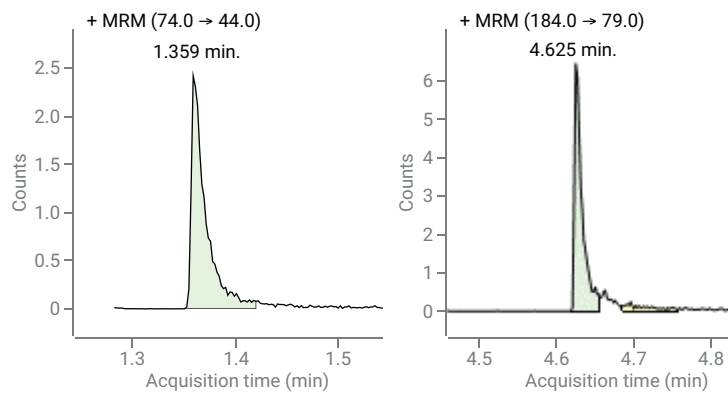


Figure 5. Quant MRM chromatograms for the low calibration standards of NDMA, 0.2 ppm (range = 0.2 to 160 ppm) and 2,4-dinitrophenol, 2 ppm (range = 2 to 160 ppm).

Conclusion

A fast and highly sensitive semivolatiles method using MRM mode has been developed for the Agilent 7000 series triple quadrupole GC/MS system. Method criteria for EPA 8270D/E are met for initial calibration over a working range of 0.02 to 160 ppm in a single 10 minute run, which is less than half of the standard analysis time. The selectivity of MRM greatly enhances method performance, and reduces the need for complicated batch review. Calibrating using one analytical method for the entire range and low method %RSDs translate to extended continuing calibration and greater laboratory productivity.

Reference

1. EPA 8270 Re-optimized for Widest Calibration Range on the 5977 Inert Plus GC/MSD, *Agilent Technologies Application Brief*, publication number 5994-0350EN, **2018**.

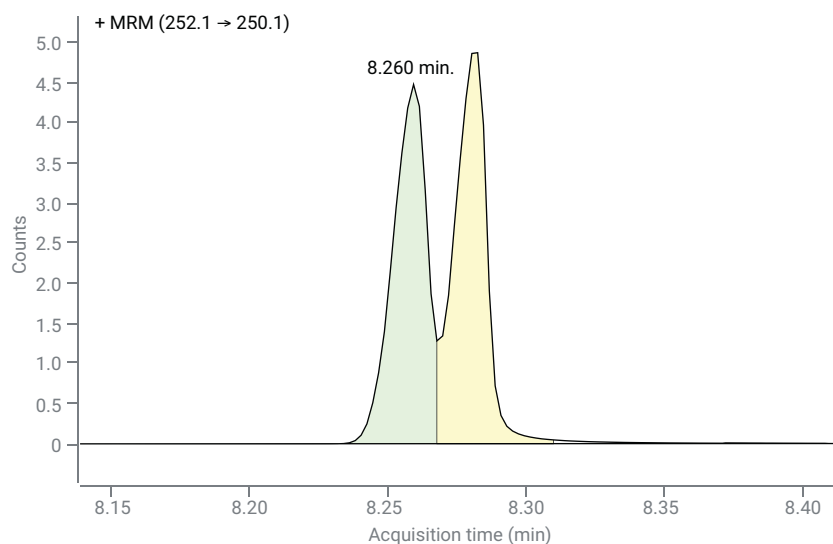


Figure 6. Benzo[b and k]fluoranthene isomer resolution at 160 ppm using optimized conditions. The split ratio is 1:20 (8 ng injected). Sufficient resolution is achieved if the height of the valley between two isomer peaks is less than 50 % of the average of the two peak heights at the midpoint concentration level (8270D/E).

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