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GC/MS: Optimized Semivolatile Organic Compounds (SVOC) Analysis in Compliance with EPA Method 8270E

Introduction

For more than 40 years, the United States Environmental Protection Agency (EPA) has monitored semivolatile organic compounds (SVOC) in wastes, soils/sediments, and groundwater via its Method 8270. This method is extensive in scope, targeting chemicals found in petroleum/soot (e.g., polycyclic aromatic hydrocarbons), plastics (e.g., phthalates), antiseptics (e.g., phenols, halobenzenes), and many other sources. Similarly extensive is the list of QC criteria for successful method performance. These criteria include one-time performance checks (e.g., initial calibration verification), 12-hour periodical performance checks (e.g., DTFPP tuning, benzidine tailing factor, DDT degradation) and batch-wise performance checks (e.g., method blank, matrix spike & duplicate, laboratory control spike).

Having undergone several revisions, EPA Method 8270 Version E (8270E) was released in 2018, introducing several important changes to the protocol. Multiple new analytes were introduced, including pyridine, 1-methylnaphthalene, and others (see compound list). Additionally, in the latest revision of Method 8270E, mention of vendor-specific columns was removed, instead directing the user toward any 5% phenyl-methylpolysiloxane or 5% phenyl-arylene dimethylpolysiloxane column.

This application note reports results from the analysis of SVOC according to the requirements of EPA Method 8270 performed with the PerkinElmer GCMS 2400™ System and PerkinElmer Elite 5MS column. The analysis demonstrates improvement upon the official method, showing faster analysis time with acceptable resolution as required by high-throughput laboratories. The GC pneumatics and oven were also assessed in this study to show high repeatability for all 87 analytes including target, surrogate, and internal standard compounds. PerkinElmer SimplicityChrom™ Chromatography Data System (CDS) Software efficiently managed the GC/MS workflow, from instrument control to data evaluation.

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Experimental

Analysis of SVOC was performed by the GC 2400 System equipped with capillary injector and single quadrupole MS Detector. All samples were chromatographed on a PerkinElmer Elite 5MS (30m by 0.25 mm I.D. x 0.25 μm df).

Table 1: Gas Chromatograph configuration and consumables.

GC Parameters		Part #
Gas Chromatograph	PerkinElmer GC 2400 with Liquid Autosampler	--
Detector	PerkinElmer MS 2400 SQ Detector	--
Column	PerkinElmer Elite 5MS, 30 m length x 0.25 mm I.D. x 0.25 μm df	N9316282
Software	PerkinElmer SimplicityChrom CDS Software	--
Carrier Gas	Grade 5 Helium, 1.2 ml/min	
Septum Purge	1 ml/min	
Split	5:1 ratio	
Oven Program	45 °C hold for 1 min; 30 °C/min to 300 °C; 2 °C/min to 310; 10 °C/min to 325 °C; hold for 4 min	
Run Time	20 min	
Injector		Part #
Type	Capillary Split/Splitless (CAP)	--
Inlet Septum	Bleed Temperature Optimized (BTO) Orange Septa, 50-pack	N9302972
Inlet Liner	Green Focus Liner with Viton O-ring, 5-pack	N6502041
Seal	Gold Seal, 10-pack	N6400901
Ferrules	Standard 15% Graphite, 85% Vespel Ferrule of 0.4 mm I.D., 10-pack	09920104
Autosampler Syringe	5 μL Precision Syringe, 6-pack	N6402584
Helium Gas Filter	Triple Filter	N9306110
Injection Volume	1 μL	--
Temperature	320 °C	--

Figure 1: The PerkinElmer GCMS 2400 System.

Table 2: List of standards used in the method.

Analytical Standards		Part #
Target Analytes	Restek™ 8270 MegaMix®, 500-1000 μg/mL in Dichloromethane	31850
Surrogates	Sigma-Aldrich™ EPA 8270 Surrogate, 4000 μg/mL in Dichloromethane	CRM47960
Internal Standards	Restek™ SV Internal Standard Mix, 2000 ug/ml in Dichloromethane	31885
MS Tuning Standard	Sigma-Aldrich™ EPA 8270 Tuning, 50 μg/mL in Dichloromethane	47387
Sample	NIST™ SRM® 1991 Mixed Coal Tar/ Petroleum in Dichloromethane	SRM1991

Table 3: Instrument operating conditions.

Mass Spectrometer Conditions	
Transfer Line	280 °C
Ion Source	330 °C
Solvent Delay	0.0-2.0 min
Scan	30-500 amu
Threshold	3

Stock Standard Preparation

To prepare the calibration curve, two stock dilution standards were prepared of target analytes at 100 μg/mL and 5.0 μg/mL, respectively, by diluting in HPLC-grade dichloromethane (VWR, Radnor, PA). Similarly, a 100 μg/mL surrogate solution was prepared in the same solvent. The 2000 μg/mL internal standard solution was used without modification.

Calibration

The 100 μg/mL stock standard of analytes was used to prepare calibration standards at 25, 10, 5.0 and 2.5 μg/mL. The 5.0 μg/mL standard was used to prepare the lower half of the calibration curve at 1.3, 0.50, 0.25, 0.13 and 0.05 μg/mL. Surrogates were calibrated over a narrower range that spanned the possible range of recovery in a spiked sample of 25, 10, 5.0, 2.5, and 1.0 μg/mL. Target analytes and surrogates were spiked into the same vials at identical concentrations. Finally, 10 μL of internal standard solution were spiked into each vial.

Acceptable calibration was measured when an analyte demonstrated a response factor (RF) with a relative standard deviation (RSD) below 20%. EPA Method 8270E permits compounds to be calibrated using the slope of the calibration curve so long as the coefficient of determination (R2) is greater than 0.990, so calibration results are presented in Table 3 for both RF RSD and R^2.

Table 4: Calibration values for the EPA Method 8270E analysis. RTs are averaged over the compound's calibration range and demonstrate exemplary precision. Seven compounds were quantified using linear calibration rather than average RF.

Compound	RT ± SD, min	Quant Ion	RF RSD	R²
1,4-dioxane-d8 (IS)	2.232 ± 0.002	96	--	--
N-nitrosodimethylamine	2.433 ± 0.005	74	13%	0.9996
Pyridine	2.459 ± 0.007	79	9.1%	0.9987
2-Fluorophenol (surr)	3.222 ± 0.002	112	5.0%	0.9989
Phenol-d6 (surr)	3.823 ± 0.001	99	5.9%	0.9992
Phenol	3.876 ± 0.002	94	13%	0.9999
Aniline	3.876 ± 0.002	93	4.4%	0.9998
Bis(2-chloroethyl)ether	3.904 ± 0.001	93	17%	0.9989
2-Chlorophenol	3.964 ± 0.003	128	3.8%	0.9985
1,3-dichlorobenzene	4.077 ± 0.000	146	5.8%	0.9989
1,4-dichlorobenzene-d4 (IS)	4.114 ± 0.000	150	--	--
1,4-dichlorobenzene	4.127 ± 0.001	146	11%	0.9976
Benzyl alcohol	4.199 ± 0.001	79	7.5%	0.9976
1,2-dichlorobenzene	4.243 ± 0.002	146	*Linear Used*	0.9985
2-methylphenol	4.271 ± 0.001	108	7.0%	0.9974
Bis(2-chloroisopropyl)ether	4.294 ± 0.002	121	11%	0.9993
N-nitroso-di-n-propylamine	4.392 ± 0.001	43	14%	0.9966
4-methyl/3-methylphenol	4.381 ± 0.001	107	4.6%	0.9994
Hexachloroethane	4.497 ± 0.002	201	14%	0.9988
Nitrobenzene-d5 (surr)	4.516 ± 0.008	82	4.6%	0.9992
Nitrobenzene	4.531 ± 0.000	77	5.2%	0.9993
Isophorone	4.709 ± 0.001	82	5.5%	0.9999
2-nitrophenol	4.776 ± 0.002	139	20%	0.9971
2,4-dimethylphenol	4.877 ± 0.000	122	5.3%	0.9995
Bis(2-chloroethoxy)methane	4.860 ± 0.002	93	6.9%	0.9981
2,4-dichlorophenol	4.957 ± 0.001	162	5.7%	0.9997
1,2,4-trichlorobenzene	5.031 ± 0.002	180	11%	0.9987
Naphthalene-d8 (IS)	5.078 ± 0.002	136	--	--
Naphthalene	5.095 ± 0.001	128	5.1%	0.9998
4-chloroaniline	5.125 ± 0.001	127	5.4%	0.9980
Hexachlorobutadiene	5.192 ± 0.002	225	5.9%	0.9996
4-chloro-3-methylphenol	5.495 ± 0.002	107	2.3%	0.9999
2-methylnaphthalene	5.642 ± 0.001	142	4.3%	0.9998
1-methylnaphthalene	5.723 ± 0.002	142	4.6%	0.9998
Hexachlorocyclopentadiene	5.777 ± 0.002	237	11%	0.9993
2,4,6-trichlorophenol	5.866 ± 0.002	196	17%	0.9999
2,4,5-trichlorophenol	5.893 ± 0.002	196	11%	0.9999
2-fluorobiphenyl (surr)	5.931 ± 0.001	172	4.6%	0.9992
2-chloronaphthalene	6.037 ± 0.002	162	4.8%	0.9993
2-nitroaniline	6.109 ± 0.002	138	18%	0.9957
1,4-dinitrobenzene	6.206 ± 0.003	168	15%	0.9994
Dimethylphthalate	6.247 ± 0.002	163	8.1%	0.9998
1,3-dinitrobenzene	6.273 ± 0.002	168	14%	0.9995

Compound	RT ± SD, min	Quant Ion	RF RSD	R^2
2,6-dinitrotoluene	6.298 ± 0.003	165	12%	0.9995
1,2-dinitrobenzene	6.346 ± 0.004	168	19%	0.9995
Acenaphthylene	6.377 ± 0.002	152	5.9%	0.9987
3-nitroaniline	6.441 ± 0.003	138	18%	0.9994
Acenaphthene-d10 (IS)	6.494 ± 0.002	164	--	--
Acenaphthene	6.501 ± 0.002	154	4.9%	0.9984
2,4-dinitrophenol	6.526 ± 0.003	184	Linear Used	0.9963
4-nitrophenol	6.555 ± 0.003	139	Linear Used	0.9981
2,4-dinitrotoluene	6.631 ± 0.002	165	17%	0.9993
Dibenzofuran	6.658 ± 0.002	168	9.2%	0.9983
2,3,5,6-tetrachlorophenol	6.722 ± 0.002	232	18%	0.9987
2,3,4,6-tetrachlorophenol	6.758 ± 0.002	232	20%	0.9995
Diethylphthalate	6.824 ± 0.001	149	19%	0.9976
Fluorene	6.941 ± 0.002	166	13%	0.9973
4-chlorophenyl phenyl ether	6.928 ± 0.002	204	5.4%	0.9996
4-nitroaniline	6.940 ± 0.003	138	19%	0.9948
4,6-dinitro-2-methylphenol	6.970 ± 0.001	198	20%	0.9976
N-nitrosodiphenylamine	7.023 ± 0.002	169	6.0%	0.9985
Azobenzene	7.061 ± 0.002	77	8.9%	0.9916
2,4,6-tribromophenol (surr)	7.137 ± 0.003	330	13%	0.9997
4-bromophenyl phenyl ether	7.332 ± 0.001	248	5.3%	0.9997
Hexachlorobenzene	7.405 ± 0.002	284	9.2%	0.9998
Pentachlorophenol	7.555 ± 0.005	266	Linear Used	0.9996
Phenanthrene-d10 (IS)	7.716 ± 0.002	188	--	--
Phenanthrene	7.736 ± 0.002	178	11%	0.9992
Anthracene	7.778 ± 0.002	178	5.8%	0.9992
Carbazole	7.902 ± 0.002	167	9.4%	0.9976
Di(n-butyl)phthalate	8.174 ± 0.002	149	19%	0.9910
Fluoranthene	8.729 ± 0.001	202	6.7%	0.9980
Pyrene	8.923 ± 0.002	202	4.1%	0.9994
P-terphenyl-d14 (surr)	9.038 ± 0.002	244	2.9%	0.9991
Butyl Benzyl Phthalate	9.453 ± 0.003	149	Linear Used	0.9971
Bis(2-ethylhexyl)adipate	9.523 ± 0.005	129	Linear Used	0.9906
Benz[a]anthracene	9.968 ± 0.003	228	20%	0.9994
Chrysene-d12 (IS)	9.997 ± 0.003	240	--	--
Chrysene	10.002 ± 0.005	228	7.6%	0.9951
Bis(2-ethylhexyl)phthalate	10.004 ± 0.007	149	14%	0.9990
Di(n-octyl)phthalate	10.744 ± 0.007	149	Linear Used	0.9929
Benzo[b]fluoranthene	11.206 ± 0.012	252	14%	0.9916
Benzo[k]fluoranthene	11.236 ± 0.008	252	9.4%	0.9998
Benzo[a]pyrene	11.658 ± 0.011	252	18%	0.9955
Perylene-d12 (IS)	11.755 ± 0.007	264	--	--
Indeno[1,2,3-cd]pyrene	13.583 ± 0.022	276	12%	0.9999
Dibenz[a,h]anthracene	13.644 ± 0.025	278	13%	0.9998
Benzo[ghi]perylene	14.077 ± 0.031	276	6.0%	0.9999

Sample Preparation

The sample, NIST SRM 1991, is comprised of a mixture of coal tar and petroleum in dichloromethane (density = 1.33 kg/L). This solution was analyzed neat with internal standard. To be consistent with 8270E protocols, surrogate was spiked to a final concentration in solution of 10 µg/mL. The sample was analyzed n=3 times.

Results & Discussion

System Performance

Performance is assessed using a 50 ng on-column injection of tuning standard. To harmonize interlaboratory mass spectrometer tuning, Method 8270 mandates a rigorous ion ratios check of DTFPP fragmentation. The "EPA Report" function in SimplicityChrom CDS Software automatically compares the results against EPA criteria and gives a visual representation of the compliance, see Figure 1. Averaged background signal (scans 1797 through 1818) is subtracted from an averaged peak signal (scans 1774 through 1783) to generate the acceptable fragmentation pattern.

Test	DFTPP 625/8270d TEST		Result	Test Passed		
Mass	Reference Mass	Relative Abundance	Criterion		Pass/Fail	
			COMBINE(1774:1783)-(1797:1818)		Pass	
51	BPI	17.3%	>= 10% and <= 80%		Pass	
68	69	1.1%	< 2%		Pass	
69	BPI	16.1%	NOT TESTED		Pass	
70	69	0.4%	< 2%		Pass	
127	BPI	32.7%	>= 10% and <= 80%		Pass	
197	198	0.1%	< 2%		Pass	
198	BPI	69.3%	= 100% or > 50%		Pass	
199	198	5.5%	>= 5% and <= 9%		Pass	
275	BPI	21.2%	>= 10% and <= 60%		Pass	
365	198	3.5%	> 1%		Pass	
441	442	17.9%	< 24% and > 0		Pass	
442	BPI	100%	= 100% or > 50%		Pass	
443	442	17.0%	>= 15% and <= 24%		Pass	

Figure 1: DTFPP ion ratios are tabulated with the EPA Report function to give a visual representation of the compliant and non-compliant results.

Tailing factors of benzidine and pentachlorophenol are used to assess inertness of the sample flow path. For a passing test, neither tailing factor may exceed a threshold value of 2.0 as measured at 10% peak height ($TF_{10\%}$). Figure 2A and 2B illustrate peak shapes of pentachlorophenol ($TF_{10\%}$ = 1.0) and benzidine ($TF_{10\%}$ = 0.8), calculated in the Automated Mass Spectral Deconvolution and Identification System, AMDIS, software.
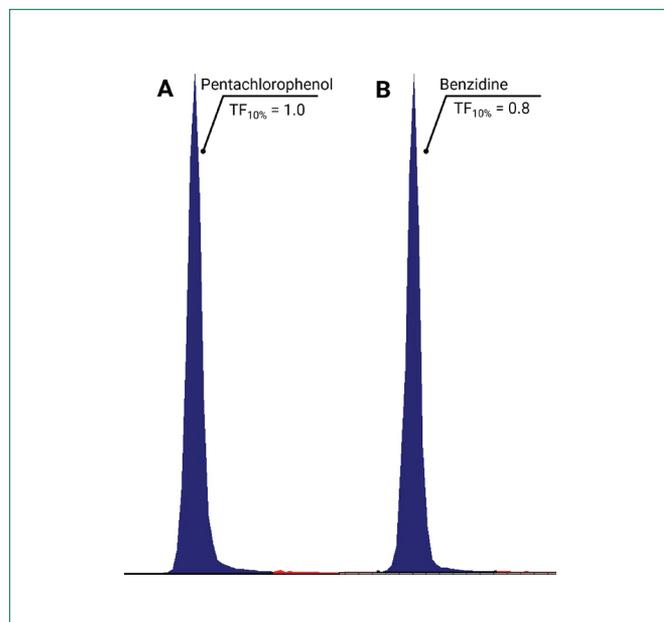

Figure 2: Excellent peak shapes of the highly-active compounds pentachlorophenol (ion 266) & benzidine (ion 184) at 50 ng-on-column show industry-leading sample flow path inertness of the GC 2400 with Elite 5MS column.

The third performance check, breakdown of DDT to DDE & DDD, is used to assess sample degradation within the injector. The EPA permits up to 20% sample breakdown, as assessed by peak area ratio. Figure 3 shows the excellent performance of the GC 2400. In total, only 1.69% of DDT was broken down, surpassing EPA-mandated limits with flying colors.
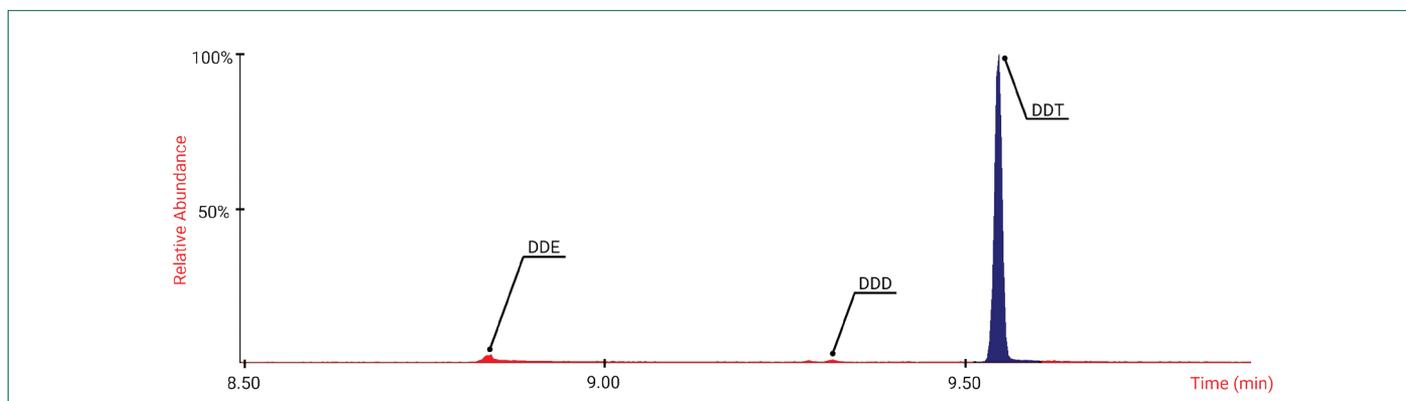
Figure 3: Minimal breakdown[1] of DDT into DDD and DDE is observed due to low reactivity within the GC 2400 System injector port.

$$^{1}\% \text{ Breakdown} = \frac{\text{Area}_{DDE} + \text{Area}_{DDD}}{\text{Area}_{DDT} + \text{Area}_{DDE} + \text{Area}_{DDD}} * 100\% = \frac{8042 + 3467}{670467 + 8042 + 3467} * 100\% = 1.69\%$$
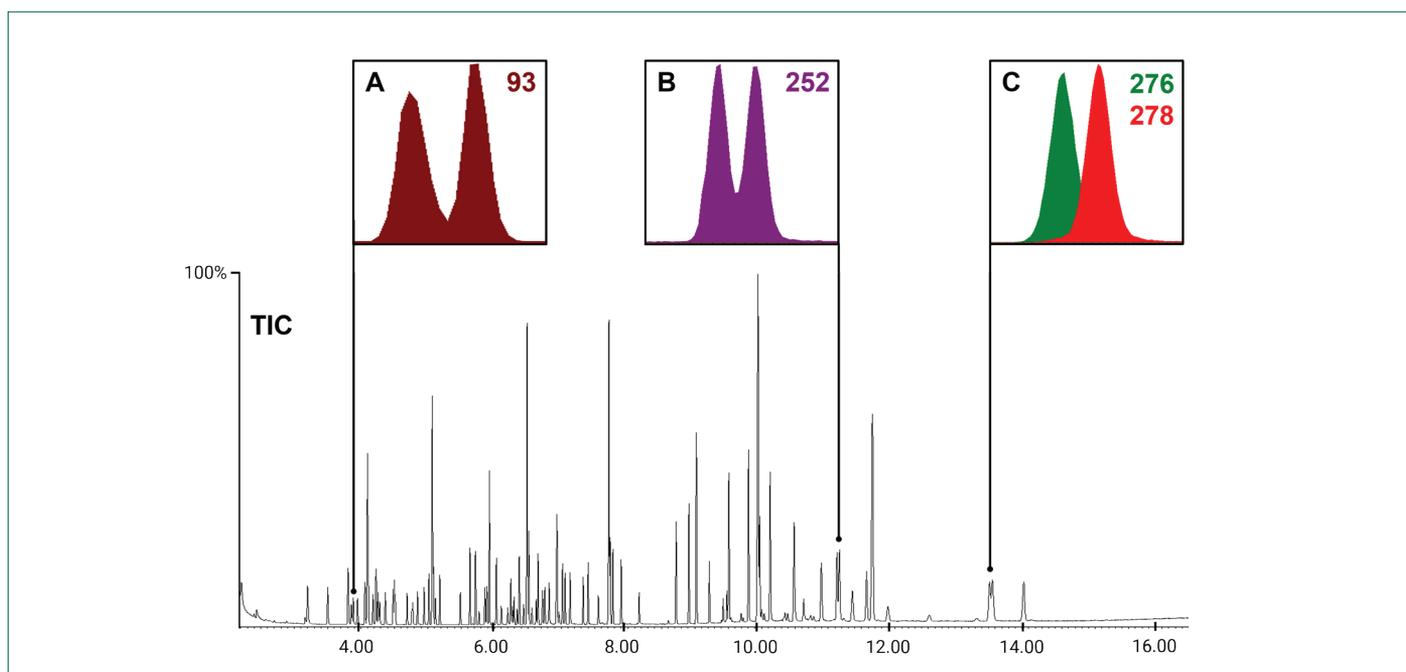

Figure 4: Total ion chromatogram (TIC, black) of the 10 µg/mL standard containing target compounds, surrogates, and internal standards all eluting within ~14 minutes. Excellent resolution of critical pairs A) aniline/bis(2-chloroethyl)ether (m/z 93, brown), B) benzo[b]fluoranthene/benzo[k]fluoranthene (m/z 252, purple) and C) dibenz[a,h] anthracene/indeno[1,2,3-cd]pyrene (m/z 276, green; m/z 278, red) is observed despite the short run-time.

Sample calibration results are presented in Table 2. The pneumatics & oven temperature controls of the GC 2400 System are extremely precise. Retention times show excellent run-to-run repeatability, with most compounds eluting within 0.003 minutes of the average across each compounds' calibration range. Method 8270E permits up to 20% RSD to quantify chemicals by response factor (RF). Of the > 80 target analytes and surrogates, only seven compounds exceeded this limit and were instead quantified by linear calibration as permitted by EPA Method 8270E, demonstrating acceptable correlation coefficients in each case (R^2).

Figure 4 presents the chromatogram of the 10 µg/mL standard along with resolution of the critical pairs aniline/bis(2-chloroethyl) ether, benzo[b]fluoranthene/benzo[k]fluoranthene, and dibenz[a,h] anthracene/indeno[1,2,3-cd]pyrene. EPA requirements for structural isomer resolution dictate a quant ion peak valley ≤50% of the average peak height; this criterion was easily met for all critical pairs in the ~14-minute elution time. Note that both aniline/ bis(2-chloroethyl)ether and dibenz[a,h]anthracene/indeno[1,2,3-cd]pyrene are not structural isomer pairs but share fragment/ molecular ions that can interfere nonetheless with quantification.

Method Accuracy

NIST standardized reference material 1991[2], a certified mixture of petroleum and coal tar in dichloromethane, was used to test proficiency of the GC 2400 System to accurately quantify compounds within complex environmental samples. In total, SRM 1991 was measured 3 times, with excellent accuracy and precision reported in Table 3. With the exception of two compounds that were determined within 25% of NIST values, every compound matched NIST values within 20% relative difference. Additionally, no bias to over/underestimate the data was observed.

Table 3: Quantitative results (mg/kg, n=3) for the NIST SRM 1991 analysis.

Compound	NIST Certified/ Reference Conc.	Observed Conc. (%diff[1])
Naphthalene	26.0 ± 1.1	21.6 ± 0.2 (-17)
2-methylnaphthalene	11.7 ± 0.5	12.5 ± 0.1 (+7)
1-methylnaphthalene	8.02 ± 0.32	8.39 ± 0.08 (+5)
Acenaphthene	6.83 ± 0.89	6.32 ± 0.07 (-7)
Fluorene	3.80 ± 1.0	3.61 ± 0.05 (-5)
Phenanthrene	12.1 ± 0.6	11.2 ± 0.2 (-8)
Anthracene	3.33 ± 0.43	3.15 ± 0.03 (-6)
Fluoranthene	3.54 ± 0.39	3.72 ± 0.08 (+5)
Pyrene	5.91 ± 0.16	6.19 ± 0.12 (+5)
Benz[a]anthracene	1.79 ± 0.21	1.38 ± 0.14 (-23)
Chrysene	1.32 ± 0.15	1.51 ± 0.09 (+14)
∑Benzofluoranthenes[2]	1.72 ± 0.12	1.29 ± 0.00 (-25)
Benzo[a]pyrene	1.33 ± 0.12	1.33 ± 0.11 (0)
Indeno[123-cd]pyrene	0.382 ± 0.030	0.421 ± 0.004 (+10)
Dibenz[ah]anthracene	0.128 ± 0.025	0.146 ± 0.007 (+14)
Benzo[ghi]perylene	0.549 ± 0.028	0.546 ± 0.013 (-1)

$$^1 \text{% diff} = \frac{\text{Conc}_{observed} - \text{Conc}_{actual}}{\text{Conc}_{actual}} * 100\%$$

NOTE: "Actual" concentration in calculation of the %diff refers to the NIST SRM concentration whilst "observed" refers to the concentration determined in this study.

[2] Sum of benzo[a]fluoranthene, benzo[b]fluoranthene, benzo[j]fluoranthene, and benzo[k]fluoranthene using the benzo[b]fluoranthene response factor.

A matrix spike and matrix spike duplicate are required by the method. These were prepared by spiking calibration standard into NIST SRM 1991 and comparing the recoveries of polycyclic aromatic hydrocarbons (PAH). Although the MS & MSD weren't taken through sample extraction, their recovery demonstrates instrument & method accuracy. On average, PAH recovery was excellent in both MS and MSD. MS recovery was measured at 96.8% ± 13.8% while MSD recovery was 96.8% ± 13.4%.

Conclusion

For the analysis of semivolatile compounds (SVOC) in compliance with EPA Method 8270E, the PerkinElmer GCMS 2400 System and Elite 5MS column offers an optimized approach enabling fast and robust performance, even for complex matrices. Using the described method conditions, every semivolatile compound can elute in just over 14 minutes, allowing more samples to be analyzed in each 12-hour periodical performance check window.

Quantitation can be achieved over a wide range of concentrations due to repeatable instrument pneumatics, inert column and injector, and consistent detector response. The high repeatability of the instrument's pneumatics and oven means that compounds reliably elute within method retention windows in highly-complex matrices.

Instrument sensitivity is high, with most compounds calibrated to the low parts-per-billion range in solution. All performance check criteria, including tailing, ion ratio, degradation, and critical pair resolution were easily surpassed.

Accurate quantification of NIST standard reference material SRM 1991, a complex sample matrix, was achieved; its associated matrix spike & matrix spike duplicate provided similarly accurate results.

The intuitive SimplicityChrom CDS Software provides a practical, customizable user experience with multifunctionality and accessibility options, supporting compliance and traceability where required by the method. In addition, the detachable touchscreen provides versatility and portability which ultimately offers time optimization for busy lab environments.

References

1　Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS); Method 8270E; United Stated Environmental Protection Agency, Revision 4, June 2018.

2　Certificate of Analysis: Standard Reference Material® 1991 Mixed Coal Tar/Petroleum Extract in Methylene Chloride; National Institute of Standards & Technology, May 2021.

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