

Analysis of Semivolatile Organic Compounds with Hydrogen Carrier Gas and HydroInert Source by Gas Chromatography/Triple Quadrupole Mass Spectrometry (GC/MS/MS)

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Abstract

Gas chromatography/mass spectrometry (GC/MS) is integral to the analysis of semivolatile organic compounds (SVOCs) in environmental matrices. Some methods have extended instrumentation to include gas chromatography/triple quadrupole mass spectrometry (GC/MS/MS) as users push towards lower detection limits. Recent pressure on the helium (He) supply has required organizations to actively investigate hydrogen (H₂) carrier gas, but most GC/MS and GC/MS/MS analyses have reduced sensitivity and hydrogenation or dechlorination in the existing mass spectrometry products. New advances in mass spectrometer design have reduced hydrogenation and dechlorination reactions in the source. The Agilent HydroInert source retains the ability to analyze a wide calibration range, for some compounds from 0.02 to 100 µg/mL, and meet the U.S. Environmental Protection Agency (EPA) method 8270 calibration criteria when using H₂ carrier gas.

Introduction

GC/MS/MS has been determined to be suitable for use with the U.S. EPA method 8270 (version 8270E) in solid waste, soil, air, and water extracts.^{1,2} Previous application notes have discussed using He carrier gas with GC/MS/MS to extend the calibration range of EPA method 8270 down to 0.02 µg/mL, while retaining the top range of the method at 160 µg/mL.³

The availability of He has been a concern for several years, but interest in transitioning to alternative carrier gases has significantly increased in recent years. However, existing mass spectrometry systems have issues with hydrogenation of some functional groups, such as nitro groups, or dechlorination of heavily chlorinated compounds. These issues would alter the mass spectrum of a peak and lead to potential misidentification of compounds, or no identification of compounds if the precursor or product ions are affected by reactions with H₂ in a source. One example is with nitrobenzene, where H₂ carrier gas and nitrobenzene exposed to metal and heat, such as in a mass spectrometer source, will hydrogenate nitrobenzene (molecular weight (MW) 123 *m/z*) to aniline (MW 93 *m/z*). This is observed by the identification of aniline at the retention time of nitrobenzene and increase in 93 *m/z* fragment intensity compared to 123 *m/z*. A newly designed extractor source called the HydroInert source, for Agilent 7000C/D/E Inert Plus triple quadrupole GC/MS systems, addresses these H₂-related issues and helps improve performance with H₂ carrier gas in GC/MS and GC/MS/MS applications, including SVOC analyses. The HydroInert source with H₂ carrier gas retains mass spectral fidelity and can allow users to continue to use existing He-based mass spectral libraries, quantitative methods, and multiple reaction monitoring transitions (MRMs).

This application note demonstrates the ability of the HydroInert source to allow the use of H₂ carrier gas, while retaining critical functional groups, such as nitro groups and halogens. Retention of mass spectral fidelity is a breakthrough for the use of H₂ carrier gas with GC/MS systems, especially for environmental analyses such as EPA method 8270. Additionally, a method for EPA 8270 has been developed that retains similar sensitivity of a He carrier gas analysis, which allows for most compounds to be calibrated between 0.02 to 100 µg/mL with less than 20% of compounds requiring linear or quadratic curve fits.

Experimental

A set of stock standards containing 120 target compounds and surrogates was selected to provide a representative mixture of acids, bases, and neutral compounds, as well as comprising various compound classes, from nitrophenols to PAHs. The nine stock standards of target analytes were at concentrations of 2,000 µg/mL; part numbers for these stock standards are as follows: SVM-160, SVM-121, SVM-122, SVM-123, SVM-124, SVM-125, SVM-126-1, SVM-127, and US-211. Pyridine was diluted from a pure standard to 1,000 µg/mL as a working standard. The surrogate standard (part number ISM-332) contained six compounds at 2,000 µg/mL, indicated in Table 1. An internal standard mixture of six deuterated PAHs was used for recovery and calibration. The stock standards were combined and diluted in dichloromethane to make a working standard at 200 µg/mL. The working standard was then diluted to form the following nominal concentrations for the targets and surrogates for calibration standards: 0.02, 0.05, 0.1, 0.2, 0.5, 0.8, 1, 2, 5, 10, 20, 35, 50, 75, and 100 µg/mL. Internal standards were added to each calibration standard at a concentration level of 40 µg/mL. Table 1 lists the compounds that were used in the study. The compound numbers in Table 1 were assigned based on retention order of the targets and surrogates, with the internal standards listed at the end of the table out of retention order.

The tuning standard (part number GCM-150), containing a mixture of benzidine, pentachlorophenol, 4,4'-dichlorodiphenyltrichloroethane (4,4'-DDT), and decafluorotriphenylphosphine (DFTPP) was diluted to a concentration of 25 µg/mL and used to verify GC flow path inertness.

A composite mixture of soils extracted with dichloromethane was prepared for EPA method 8270 analysis. The mixture is a representative matrix residue that is typically encountered in the lab and was procured from Pace Analytical (Mt. Juliet, TN).

Table 1. Target, surrogates, and internal standards.

No.	Compound	No.	Compound	No.	Compound
1	N-Nitrosodimethylamine (NDMA)	43	4-Chloro-3-methyl phenol	85	Pentachloronitrobenzene
2	Pyridine	44	2-Methylnaphthalene	86	4-Aminobiphenyl
3	2-Picoline	45	1,2,4,5-Tetrachlorobenzene	87	Propylamide
4	N-Nitroso-N-methylethylamine	46	Hexachlorocyclopentadiene	88	Phenanthrene
5	Methyl methanesulfonate	47	2,4,6-Trichlorophenol	89	Dinoseb
6	2-Fluorophenol (surrogate)	48	2,4,5-Trichlorophenol	90	Disulfoton
7	N-Nitrosodiethylamine	49	2-Fluorobiphenyl (surrogate)	91	Anthracene
8	Ethyl methanesulfonate	50	1-Chloronaphthalene	92	Parathion-methyl
9	Phenol-d ₆ (surrogate)	51	2-Chloronaphthalene	93	Di-n-butyl phthalate
10	Phenol	52	2-Nitroaniline	94	4-Nitroquinoline-1-oxide
11	Aniline	53	Dimethyl phthalate	95	Parathion
12	Bis(2-chloroethyl)ether	54	Acenaphthylene	96	Fluoranthene
13	2-Chlorophenol	55	2,6-Dinitrotoluene	97	Benzidine
14	1,3-Dichlorobenzene	56	3-Nitroaniline	98	Pyrene
15	1,4-Dichlorobenzene	57	Acenaphthene	99	p-Terphenyl-d ₁₄ (surrogate)
16	Benzyl alcohol	58	2,4-Dinitrophenol	100	Aramite I
17	1,2-Dichlorobenzene	59	Pentachlorobenzene	101	Aramite II
18	2-Methylphenol (o-cresol)	60	4-Nitrophenol	102	4-Dimethylaminoazobenzene
19	Bis(2-Chloro-1-methylethyl)ether	61	Dibenzofuran	103	Chlorobenzilate
20	4-Methylphenol (p-cresol)	62	2,4-Dinitrotoluene	104	3,3'-Dimethyl benzidine
21	N-Nitrosopyrrolidine	63	1-Naphthylamine	105	Famphur
22	Acetophenone	64	2,3,4,6-Tetrachlorophenol	106	Butyl benzyl phthalate
23	4-Nitrosomorpholine	65	2-Naphthylamine	107	Benzo[a]anthracene
24	N-Nitrosodi-n-propylamine	66	Diethyl phthalate	108	3,3'-Dichlorobenzidine
25	o-Toluidine	67	Fluorene	109	Chrysene
26	Hexachloroethane	68	Thionazin	110	Bis(2-ethylhexyl) phthalate
27	Nitrobenzene-d ₅ (surrogate)	69	5-Nitro-o-toluidine	111	Di-n-octyl phthalate
28	Nitrobenzene	70	4-Chlorophenyl phenyl ether	112	Benzo[b]fluoranthene
29	N-Nitrosopiperidine	71	4-Nitroaniline	113	7,12-Dimethylbenz[a]anthracene
30	Isophorone	72	2-methyl-4,6-dinitrophenol (DNOC)	114	Benzo[k]fluoranthene
31	2-Nitrophenol	73	N-Nitrosodiphenylamine	115	Benzo[a]pyrene
32	2,4-Dimethylphenol (2,4-xlenol)	74	Diphenylamine	116	3-Methylcholanthrene
33	Benzoic acid	75	Azobenzene	117	Dibenz[a,j]acridine
34	Bis(2-Chloroethoxy)methane	76	2,4,6-Tribromophenol (surrogate)	118	Indeno[1,2,3-cd]pyrene
35	2,4-Dichlorophenol	77	Sulfotep	119	Dibenz[a,h]anthracene
36	1,2,4-Trichlorobenzene	78	Dimethoate	120	Benzo[g,h,i]perylene
37	Naphthalene	79	Diallate I	121	1,4-Dichlorobenzene-d ₄ (internal standard)
38	4-Chloroaniline	80	Phorate	122	Naphthalene-d ₈ (internal standard)
39	2,6-Dichlorophenol	81	Phenacetin	123	Acenaphthalene-d ₁₀ (internal standard)
40	Hexachlorobutadiene	82	4-Bromophenyl phenyl ether	124	Phenanthrene-d ₁₀ (internal standard)
41	p-Phenylenediamine	83	Hexachlorobenzene	125	Chrysene-d ₁₂ (internal standard)
42	N-Nitrosodi-n-butylamine	84	Pentachlorophenol	126	Perylene-d ₁₂ (internal standard)

Instrumental methods

The Agilent 8890B GC was configured with a multimode inlet (MMI) and an Agilent J&W DB-5ms Ultra Inert GC column (part number 121-5522UI) interfaced with an Agilent 7000E Inert Plus triple quadrupole GC/MS system and an Agilent HydroInert source. Table 2 summarizes the GC/MS instrumentation and consumables used in this study. The GC and MS/MS method parameters (Table 3) have been optimized to provide a 12-minute method, while retaining the required resolution for isomer pairs and following the EPA 8270 guidelines for method parameters. The mass spectrometer was operated in electron ionization mode and was autotuned with the etune algorithm. Check tunes were run periodically to verify that the ion ratios and mass positions of the tune calibrant, perfluorotributylamine (PFTBA), were within tolerances. The analytical method used an Agilent Ultra Inert low pressure drop inlet liner with the 20:1 split injection and an Agilent J&W DB-5ms Ultra Inert GC column, 20 m × 0.18 mm, 0.18 μm; this column choice is preferred with H₂ carrier gas to maintain reasonable inlet pressures, as well as requiring a split injection to avoid overloading the column. Additionally, the split injection is better for the GC/MS/MS, which is commonly used for trace analyses with target analyte concentrations below 1 μg/mL. The 20:1 split drops the 100 μg/mL highest standard down to 5 μg/mL on column. With the ramped temperature of the inlet, H₂ carrier gas, and dichloromethane solvent, it is critical to verify extracted samples do not contain water; extraction steps must include a step to remove residual water to reduce the risk of generating hydrochloric acid in the inlet and causing damage to the instrument and consumables. The acquisition method was retention time locked to the internal standard, acenaphthene-d₁₀, to maintain consistent retention times across column changes and different instruments, which is critical. The final oven temperature hold time was tested at 2 minutes and 2.7 minutes; benzo[g,h,i]perylene eluted at 10.13 minutes and the 2-minute final hold would result in a method run time of 11.3 minutes, if cycle time is a concern. No quench gas is used with H₂ carrier gas; disconnect the He tubing from the back of the electronic pressure control module. Data was collected using dynamic MRM (dMRM) for more efficient use of the GC/MS/MS analytical time.

MRM transitions from previous application notes and methods were leveraged for this work to reduce the development of MRM transitions, but collision energies were reoptimized using Agilent MassHunter Optimizer. Additionally, some compounds were not listed in previous work and MassHunter Optimizer was used to identify the best MRM transitions and collision energies for the following compounds: 2,6-dichlorophenol, N-nitrosomethylethylamine, and N-nitrosomorpholine. For the GC/MS tuning mixture runs, a scan mode acquisition method was used, as DFTPP, DDT, and the breakdown products of DDT were not in the MRM acquisition method.

Instrumentation

Table 2. GC and MSD instrumentation and consumables.

Parameter	Value
GC	Agilent 8890 GC system
MS	Agilent 7000E Inert Plus triple quadrupole GC/MS with the Agilent HydroInert source
Extraction Lens	9 mm HydroInert
Syringe	Agilent Blue Line autosampler syringe, 10 μL, PTFE-tip plunger (p/n G4513-80203)
Column	Agilent J&W DB-5ms Ultra Inert GC column, 20 m × 0.18 mm, 0.18 μm (p/n 121-5522UI)
Inlet Liner	Agilent Ultra Inert inlet liner, low pressure drop, glass wool (p/n 5190-2295)

Instrument conditions

Table 3. GC and MSD instrument conditions.

Parameter	Value
Injection Volume	1 μL
Multimode Inlet	Split 20:1 250 °C (hold 0.3 min) ramp 200 °C/min to 350 °C (hold for run length) Postrun: 350 °C/min with 100 mL/min split flow
Column Temperature Program	40 °C (hold 0 min), 30 °C/min to 320 °C (hold 2 to 2.7 min*) Post run: 320 °C hold for 2 min
Carrier Gas and Flow Rate	H ₂ at 1.2 mL/min**, constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Collision Gas and Flow Rate	Nitrogen, 1.5 mL/min
Quench Gas	No quench gas is used with H ₂ carrier gas
EMV Mode	Gain factor
Gain Factor	1 (optimized for each system)
Scan Type	dMRM

* Oven hold time set to 2 minutes would generate a run time of 11.3 minutes; benzo[g,h,i]perylene eluted at 10.13 minutes.

** RT locking may result in a different flow rate on different instruments.

Results and discussion

GC/MS tuning mix

Even though the GC/MS/MS system can be and was tuned with the manufacturer's recommended tune, which is the etune default for Agilent 7000 series triple quadrupole GC/MS systems, the DFTPP ion ratio criteria from Table 3 of EPA method 8270E were used to test the HydroInert source with H₂ carrier gas.^{1,2} Table 4 summarizes the relative abundances of the DFTPP ion ratios at 25 µg/mL, the method criteria, and if the measured relative abundances matched the criteria, where all measured relative abundances pass the 8270E ion ratio criteria.

There is always concern of inlet and column cleanliness for EPA method 8270 to work, no matter the carrier gas; DDT, pentachlorophenol, and benzidine are used to track inlet breakdown and column health. Increased DDT breakdown indicates a need for inlet maintenance, while increasing tailing factors of benzidine and pentachlorophenol inform the user to trim or change the column. With the introduction of H₂ carrier gas, users may be worried about increased reactions of active compounds such as DDT in the inlet; the recommendation is to lower the inlet temperature to 230 to 250 °C and use a temperature-programmable inlet, such as the MMI, to protect the active compounds, while still being able to increase the temperature to 320 or 350 °C and drive out the PAHs. In this note, we have used the MMI.

Reviewing the results of the GC/MS tuning mixture for DDT breakdown and compound tailing factors from a scan mode run, the DDT (%) breakdown was 1.4%, the pentachlorophenol tailing factor was 1.0, and the benzidine tailing factor was 1.4. All values are within the EPA method 8270 criteria of <20% DDT breakdown and tailing factors <2.0.

Initial calibration

Figure 1 displays a total ion chromatogram (TIC) for the separation of 120 target analytes and six internal standards. A multipoint calibration was performed with 15 concentration levels from 0.02 to 100 µg/mL, and the relative response factor (RF) was determined for each compound at each calibration level. The average RF was calculated for the calibration curve of each compound along with the relative standard deviation (%RSD). The preferred passing criteria for EPA method 8270 is an average RF %RSD less than 20%; if not attainable with six or more calibration levels, a linear curve fit requires an R² value of 0.990 or greater, as does a quadratic curve fit. Accuracy of the lowest data point must be within 30% of the estimated concentration.

Table 4. DFTPP ions, abundance criteria from EPA method 8270E², measured relative abundance and pass/fail of the relative abundance for the Agilent HydroInert source in a GC/MS/MS system with H₂ carrier gas.

Target Mass (m/z)	Ion Abundance Criteria	Measured Relative Abundance	Pass/Fail
68	<2% of 69 m/z	0 %	Pass
69	Present	36.4 %	Pass
70	<2% of 69 m/z	1.1 %	Pass
197	<2% of 198 m/z	0 %	Pass
198	Base peak or present	100 % (base peak)	Pass
199	5 to 9% of 198 m/z	7.0 %	Pass
365	>1% of Base peak	1.8 %	Pass
441	<150% of 443 m/z	51.8 %	Pass
442	Base peak or present	46.7% (base peak)	Pass
443	15 to 24% of 442 m/z	21.9 %	Pass

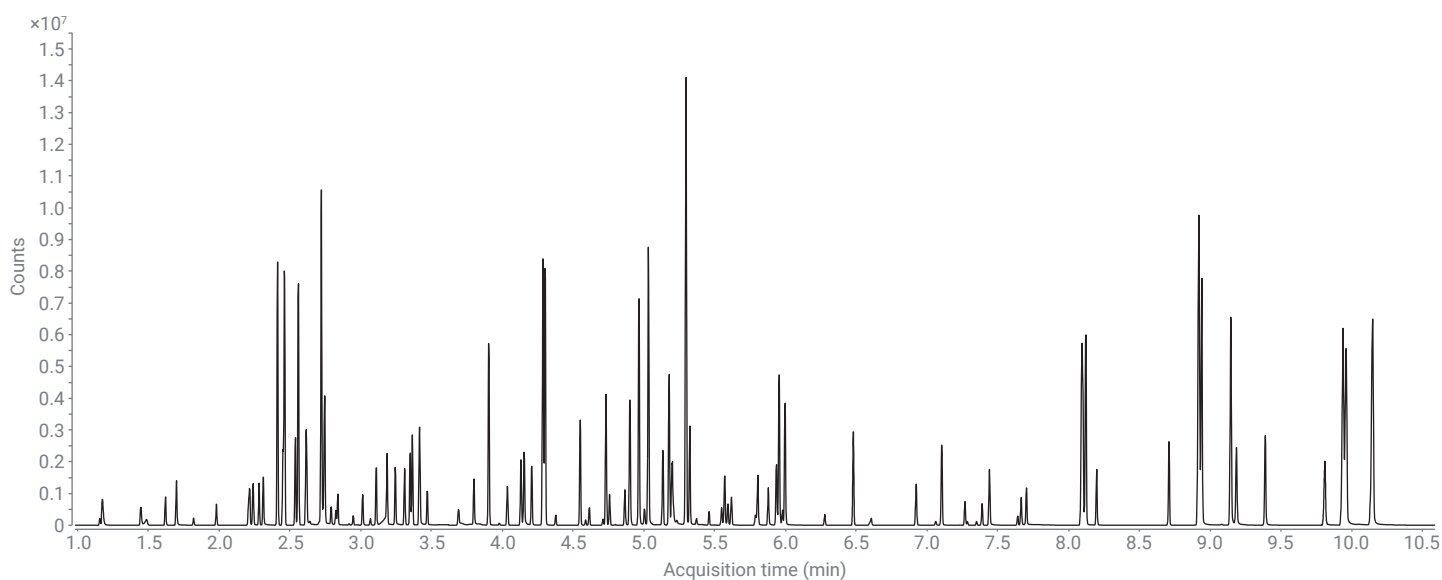


Figure 1. TIC of the 50 µg/mL calibration standard showing separation in under 10 minutes.

Critical pair resolution

With the shorter method time and different column, critical pair resolution above 50% was verified for phenanthrene and anthracene (MRM transition of 178.1 → 152.1 *m/z*), benz[a]anthracene and chrysene (228.1 → 226.1 *m/z*), and benzo(b)fluoranthene and benzo(k)fluoranthene (252.1 → 250.1 *m/z*). All three isomer pairs are shown in Figure 2 at a midlevel concentration of 5 µg/mL; phenanthrene and anthracene (Figure 2A) have baseline resolution, benz[a]anthracene and chrysene (Figure 2B) are nearly baseline resolved, and benzo(b)fluoranthene and benzo(k)fluoranthene (Figure 2C) are ~70% resolved, satisfying the EPA method 8270 criteria.

Mass spectral fidelity

A common concern of using H₂ carrier gas is the reactivity of H₂ at active sites, such as the hot metal inside of a source, which can cause hydrogenation and dechlorination reactions. Compound transformations, such as hydrogenation of nitro functional groups to amine groups could cause low or no response for MRM transitions that have been identified with He carrier gas and result in no identification or misidentification of a compound in a sample. Retention of existing method MRM transitions is preferred to reduce method development work. With the HydroInert source, users can retain the same MRM transitions with H₂ carrier

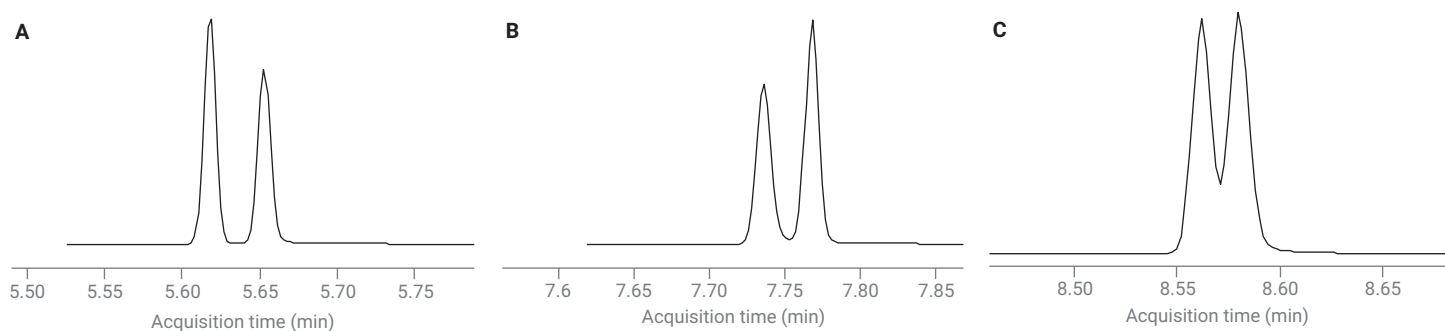


Figure 2. Midlevel standard (5 µg/mL) MRM transition extracted ion chromatograms (EICs) for critical isomer pairs: (A) phenanthrene and anthracene (MRM transition of 178.1 → 152.1 *m/z*); (B) benz[a]anthracene and chrysene (228.1 → 226.1 *m/z*); (C) benzo(b)fluoranthene and benzo(k)fluoranthene (252.1 → 250.1 *m/z*).

gas that they developed with He systems. Retention times and collision energies must be re-evaluated, especially for retention times if column dimensions and oven temperature ramps are altered. The compound list above has several nitro compounds and heavily chlorinated compounds that would be susceptible to reactions with H₂ in the normal extractor source, including nitrobenzene, pentachlorophenol, hexachlorobenzene, and pentachloronitrobenzene. We can observe retention of functional groups by verifying the MRM transition EICs exist and the expected ratios between the quantifier and qualifier MRM transitions. If the ratios for the qualifier transitions (compared to the quantifier transition) are close to 100%, reactions with H₂ are not occurring. Missing, very low, or very high MRM transition ratios would indicate reaction with H₂. Figure 3 shows a set of overlays of the MRM transitions for parathion (Figure 3A), a compound with a nitro group, and hexachlorobenzene (Figure 3B), a heavily chlorinated compound. Figures 3A and 3B each have the transition ratio percentages listed in the top-left corner. For parathion, if the nitro functional group was hydrogenated to an amine group, the 291 → 109 transition would be lower in abundance and ratio to the quantifier transition, as the MW would be 259 *m/z*, instead of 291 *m/z*. As shown in Figure 3A, the transition ratios were at 100%, indicating retention of the nitro functional group. For hexachlorobenzene, dechlorination would result in higher abundance of the 249 → 214 transition and lower abundance at 284 → 214 transition; however, Figure 3B displays retention of the expected ratio between these two transitions at 100%, and no significant dechlorination occurred.

Calibration data

Of 120 compounds, six compounds required linear fits and 10 quadratic fits were required. Table 5 summarizes the calibration results for the 120 target compounds and surrogates with average response factor (RF) %RSD values, the curve fit and R² value, if required, and the lowest and highest concentration level, if the values are different than the extended calibration range, 0.02 to 100 µg/mL. Over 86% of the 120 compounds pass the calibration criteria with an average RF %RSD below 20%. Of the 120 compounds, 13 compounds (<11%) had a calibration range narrower than the normal EPA method 8270 range of 0.1 to 100 µg/mL, but all still passed EPA method 8270E criteria by at least seven calibration levels or more. Looking at the previous work using EPA method 8270E and GC/MS/MS with He carrier gas, eight compounds required curve fits to pass the calibration criteria.³ An increase in linear and quadratic fits is predictable since H₂ is more reactive than He. Also, the inlet is initially set to a lower temperature to avoid formation of hydrochloric

acid in the presence of higher temperatures and water in the inlet, whether from carrier gas or the sample extraction procedure. In both He and the H₂ carrier gas results, bis(2-ethylhexyl)phthalate and di-*n*-octyl phthalate required quadratic fits to pass the calibration criteria. However, some of the compounds requiring curve fits were different between the two data sets. For example, N-nitrosodipropylamine passed with average RF %RSD of 12.3% for the He data, but required a linear fit for the H₂ carrier gas with the HydroInert source. N-nitrosodimethylamine (NDMA) required a linear fit from 0.2 to 100 µg/mL for the He-generated data, but passed

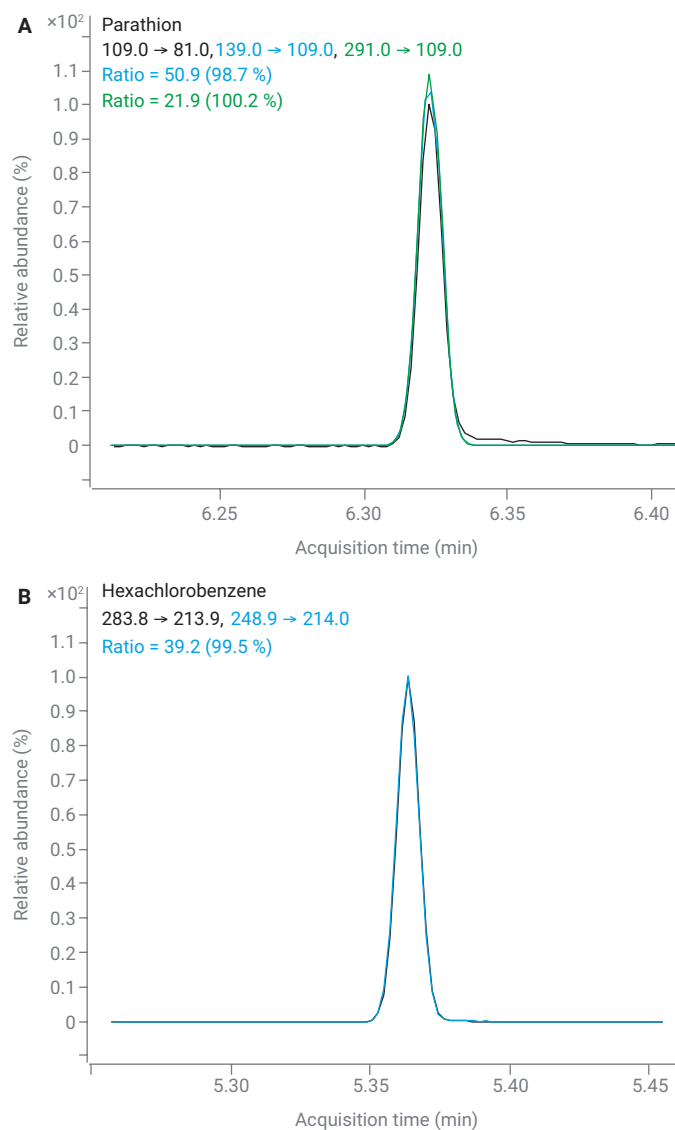


Figure 3. Overlays of MRM transition EICs for (A) parathion and (B) hexachlorobenzene, when using H₂ carrier gas and the Agilent HydroInert source on a GC/MS/MS system, showing retention of key functional groups in the presence of H₂.

Table 5. Initial calibration results for 120 target compounds and surrogates for H₂ carrier gas and the Agilent HydroInert source in GC/MS/MS for EPA method 8270.

Name	RT (min)	Avg. RF	Average RF %RSD	Curve Fit R ²	Curve Fit	Low Standard (µg/mL)	High Standard (µg/mL)
						Default is 0.02 to 100 µg/mL	
NDMA	1.1613	0.074	17.28			0.02	100
Pyridine	1.1832	0.487	16.17			0.05	100
2-Picoline	1.4508	0.154	11.23			0.05	100
N-Nitroso-N-methylethylamine	1.4893	0.101	13.58			0.02	100
Methyl methanesulfonate	1.6215	0.385	6.18			0.02	100
2-Fluorophenol (surrogate)	1.6962	0.515	12.02			0.02	100
N-Nitrosodiethylamine	1.8184	0.069	15.15			0.02	100
Ethyl methanesulfonate	1.9794	0.307	7.28			0.02	100
Phenol-d ₆ (surrogate)	2.2064	0.287	9.81			0.02	100
Phenol	2.2135	0.278	12.45			0.05	100
Aniline	2.2394	0.638	11.65			0.02	100
Bis(2-chloroethyl)ether	2.2817	0.538	4.95			0.02	100
2-Chlorophenol	2.3106	0.536	11.28			0.02	100
1,3-Dichlorobenzene	2.413	0.922	2.68			0.02	100
1,4-dichlorobenzidine-d ₄ (ISTD)	2.450		3.46			0.02	100
1,4-Dichlorobenzene	2.461	0.917	3.36			0.02	100
Benzyl alcohol	2.5379	0.388	14.57			0.02	100
1,2-Dichlorobenzene	2.5582	0.879	2.65			0.02	100
2-Methylphenol (o-cresol)	2.6123	0.524	7.24			0.02	100
Bis(2-chloro-1-methylethyl)ether	2.639	0.031	7.60			0.02	100
N-Nitrosopyrrolidine	2.7006	0.029	14.89			0.05	100
4-Methylphenol (p-cresol)	2.7173	0.738	8.05			0.02	100
Acetophenone	2.7202	0.971	7.46			0.05	100
N-Nitrosodi-n-propylamine	2.722	0.027		0.9951	Linear	0.1	100
4-Nitrosomorpholine	2.7331	0.097	16.61			0.02	100
o-Toluidine	2.741	0.735	9.62			0.02	100
Hexachloroethane	2.7897	0.150	6.42			0.02	100
Nitrobenzene-d ₅ (surrogate)	2.8228	0.074	11.46			0.02	100
Nitrobenzene	2.837	0.259	12.83			0.05	100
N-Nitrosopiperidine	2.9445	0.049	15.16			0.1	100
Isophorone	3.0114	0.251	9.29			0.02	100
2-Nitrophenol	3.0661	0.067	16.02			0.02	100
2,4-Dimethylphenol (2,4-xylenol)	3.107	0.441	7.45			0.02	100
Benzoic acid	3.1093	0.202		0.9965	Linear	2	100
bis(2-Chloroethoxy)methane	3.186	0.741	6.02			0.02	100
2,4-Dichlorophenol	3.2418	0.420	17.51			0.02	100
1,2,4-Trichlorobenzene	3.3073	0.577	7.97			0.02	100
Naphthalene-d ₈ (ISTD)	3.348		3.25			0.02	100
Naphthalene	3.3634	0.902	3.21			0.02	100
4-Chloroaniline	3.4127	0.558	5.69			0.02	100
2,6-Dichlorophenol	3.4162	0.353	15.57			0.02	100
Hexachlorobutadiene	3.4689	0.410	4.92			0.02	100

Name	RT (min)	Avg. RF	Average RF %RSD	Curve Fit R ²	Curve Fit	Low Standard (µg/mL)	High Standard (µg/mL)
						Default is 0.02 to 100 µg/mL	
<i>p</i> -Phenylenediamine	3.6874	0.232	11.54			0.1	100
N-Nitrosodi- <i>n</i> -butylamine	3.6903	0.069	8.48			0.02	100
4-Chloro-3-methylphenol	3.7999	0.372	11.05			0.02	100
2-Methylnaphthalene	3.9022	1.689	4.44			0.02	100
Hexachlorocyclopentadiene	4.0322	0.034	18.12			0.02	100
1,2,4,5-Tetrachlorobenzene	4.0348	0.230	6.13			0.02	100
2,4,6-Trichlorophenol	4.1305	0.171	19.08			0.02	100
2,4,5-Trichlorophenol	4.1537	0.255	15.58			0.02	100
2-Fluorobiphenyl (surrogate)	4.2061	0.364	3.16			0.02	100
1-Chloronaphthalene	4.2848	0.810	4.80			0.02	100
2-Chloronaphthalene	4.2998	0.784	4.74			0.02	100
2-Nitroaniline	4.3763	0.060	15.70			0.02	100
Dimethyl phthalate	4.5458	0.799	10.18			0.02	100
2,6-Dinitrotoluene	4.5829	0.034	9.97			0.02	100
Acenaphthylene	4.6136	0.146	7.06			0.02	100
3-Nitroaniline	4.7069	0.034	16.75			0.1	100
Acenaphthene-d ₁₀ (ISTD)	4.731		3.03			0.02	100
Acenaphthene	4.7548	0.184	2.87			0.02	100
2,4-Dinitrophenol	4.801	0.006		0.9988	Linear	1	100
Pentachlorobenzene	4.8623	0.149	4.46			0.02	100
4-Nitrophenol	4.8639	0.055	15.34			0.1	100
Dibenzofuran	4.8969	1.389	4.27			0.02	100
2,4-Dinitrotoluene	4.9036	0.030	17.05			0.1	100
1-Naphthylamine	4.9616	0.746	10.88			0.02	100
2,3,4,6-Tetrachlorophenol	5.0024	0.066	18.19			0.1	75
2-Naphthylamine	5.0276	0.906	7.70			0.02	100
Diethyl phthalate	5.1254	0.583	12.91			0.1	100
Fluorene	5.1741	1.433	4.42			0.02	100
Thionazin	5.1855	0.037		0.9992	Quadratic	0.05	100
5-Nitro- <i>o</i> -toluidine	5.1925	0.052	17.22			0.2	100
4-Chlorophenyl phenyl ether	5.1941	0.363	8.62			0.02	100
4-Nitroaniline	5.1986	0.111	15.16			0.1	100
2-Methyl-4,6-dinitrophenol (DNOC)	5.2271	0.009		0.9992	Linear	0.2	75
N-Nitrosodiphenylamine	5.2922	2.207	5.19			0.02	100
Diphenylamine	5.2923	2.697	5.23			0.02	100
Azobenzene	5.3216	0.966	19.48			0.1	100
2,4,6-Tribromophenol (surrogate)	5.3661	0.048	18.64			0.05	100
Sulfotep	5.4547	0.046		1.0000	Quadratic	0.1	100
Dimethoate	5.4556	0.004		0.9996	Quadratic	0.1	100
Diallate I	5.5446	0.056		0.9995	Quadratic	0.2	100
Phorate	5.5454	0.112	19.23			0.05	50
Phenacetin	5.5584	0.395		0.9926	Linear	0.2	100
4-Bromophenyl phenyl ether	5.591	0.214	4.60			0.02	100
Hexachlorobenzene	5.6139	0.411	3.63			0.02	100

Name	RT (min)	Avg. RF	Average RF %RSD	Curve Fit R ²	Curve Fit	Low Standard (µg/mL)	High Standard (µg/mL)
						Default is 0.02 to 100 µg/mL	
Pentachlorophenol	5.785	0.106		0.9996	Quadratic	0.5	100
Pentachloronitrobenzene	5.7933	0.053	17.34			0.02	100
4-Aminobiphenyl	5.8011	0.415	7.12			0.02	100
Propyzamide	5.8731	0.228	18.96			0.1	75
Phenanthrene-d ₁₀ (ISTD)	5.936		2.96			0.02	100
Phenanthrene	5.9516	1.117	6.24			0.02	100
Dinoseb	5.9596	0.046	16.84			0.2	100
Disulfoton	5.9761	0.189		0.9999	Quadratic	0.05	100
Anthracene	5.9921	0.857	3.53			0.02	100
Parathion-methyl	6.2746	0.068	18.32			0.02	100
Di- <i>n</i> -butyl phthalate	6.4745	0.567	19.97			0.05	100
4-Nitroquinoline-1-oxide	6.5908	0.011	19.12			0.2	75
Parathion	6.6037	0.032	16.40			0.05	100
Fluoranthene	6.9204	0.344	4.85			0.02	100
Benzidine	7.0591	0.029	17.04			0.1	100
Pyrene	7.1006	0.361	4.52			0.02	100
<i>p</i> -Terphenyl-d ₁₄ (surrogate)	7.2656	0.141	3.33			0.02	100
Aramite I	7.2822	0.014	12.68			0.02	100
Aramite II	7.3467	0.013	11.52			0.02	100
4-Dimethylaminoazobenzene	7.3855	0.053		0.9989	Quadratic	0.05	100
Chlorobenzilate	7.4376	0.171	19.35			0.02	75
Famphur	7.6348	0.061	11.33			0.02	50
3,3'-Dimethyl benzidine	7.6608	0.097	11.45			0.05	100
Butyl benzyl phthalate	7.6991	0.155		0.9986	Quadratic	0.05	100
Benz[a]anthracene	8.0875	1.018	9.47			0.05	100
3,3'-Dichlorobenzidine	8.0933	0.075	16.78			0.1	100
Chrysene-d ₁₂ (ISTD)	8.100		3.61			0.02	100
Chrysene	8.1151	0.437	6.10			0.02	100
bis(2-Ethylhexyl) phthalate	8.1936	0.250		0.9992	Quadratic	0.05	100
Di- <i>n</i> -octyl phthalate	8.7044	0.470		0.9991	Quadratic	0.05	100
Benzo[b]fluoranthene	8.9096	1.258	3.89			0.02	100
7,12-Dimethylbenz[a]anthracene	8.9135	0.603	14.52			0.02	100
Benzo[k]fluoranthene	8.9307	1.258	4.48			0.02	100
Benzo[a]pyrene	9.1396	0.922	11.99			0.02	100
Perylene-d ₁₂ (ISTD)	9.183		5.97			0.02	100
3-Methylcholanthrene	9.3835	0.455	19.13			0.02	100
Dibenz[a,j]acridine	9.7986	0.375		0.9923	Linear	0.2	100
Indeno[1,2,3-cd]pyrene	9.9277	0.961	12.31			0.02	100
Dibenz[a,h]anthracene	9.9494	0.140	10.41			0.02	100
Benzo[g,h,i]perylene	10.133	1.265	4.92			0.02	100

calibration criteria across the full default range of 0.02 to 100 µg/mL, with an average RF %RSD of 17.3% using the H₂ carrier gas with the Hydrolnert source.³ Individual differences in specific compounds are expected since the method was moved from an inert gas to a more reactive gas, and changes were made to the inlet and oven parameters.

During method development, the starting MMI temperature was varied to test for the best results across the entire run time. The best results were generated when the MMI was ramped up from 250 to 350 °C in this method. The inlet was also tested starting at a lower inlet temperature of 230 °C, which had better results for some of the earlier-eluting sensitive compounds, such as benzoic acid, but the later-eluting PAHs did not perform as well with respect to the linear ranges, and there was some risk of carryover. The specific inlet parameters should be optimized by the user for their analysis needs.

Sensitivity loss with H₂ carrier gas and existing mass spectrometer systems has been well reported. Due to this concern, particular attention was paid to the calibration range and verifying that most compounds were able to achieve the same calibration range as previous He analyses. On the topic of sensitivity, 77 compounds were analyzed in a previous application for EPA method 8270 with He carrier gas on GC/MS/MS.³ Comparing these compounds with the same set using the Hydrolnert source and H₂ carrier gas (also GC/MS/MS), only 8 more compounds required linear or quadratic fits than the He data. As is normal, benzoic acid required a linear fit with a calibration range of 2 to 100 µg/mL, where the curve fit and calibration range was the same between He and H₂ data. For 2,4-dinitrophenol, both analyses required linear fits but the H₂ data had a narrower range, starting at 1 µg/mL instead of 0.5 µg/mL

for He. When starting at 230 °C for the inlet temperature, the 2,4-dinitrophenol calibration range started at 0.5 µg/mL; if 2,4-dinitrophenol detection is most critical, then the method should be built for this sensitive compound. Pentachlorophenol had the same curve fit, quadratic, and a calibration range of 0.5 to 100 µg/mL for both H₂ with Hydrolnert source and He results. On the other hand, 4-nitrophenol passed calibration criteria with an average RF %RSD of 17.4% with a 0.1 to 100 µg/mL range for the H₂ analysis, while the He results required a linear fit from 5 to 160 µg/mL. Also, benzidine was routinely identifiable in all analyses with H₂ and Hydrolnert source in the GC/MS/MS; in this specific method, the average RF %RSD was 17.5% for the full extended calibration range from 0.02 to 100 µg/mL, while the benzidine data was not included in the He results. Another pair of examples of extended calibration range with the H₂ and Hydrolnert data can be shown with bis(2-ethylhexyl) phthalate and di-*n*-octylphthalate. Both phthalate compounds had a wider calibration range of 0.05 to 100 µg/mL with a quadratic fit for the H₂ data, compared to the He quadratic fit from 0.5 to 100 µg/mL. Reviewing the internal standards, the average RF %RSDs are all below 6%, indicating consistent performance for the H₂ carrier gas, Hydrolnert source, and GC/MS/MS, and no issues with hydrogenation of deuterated compounds. The deuterated surrogate compounds, nitrobenzene-d₅, phenol-d₆, and *p*-terphenyl-d₁₄, further support the retention of deuterium bonds with average RF %RSDs below 12% for the extended calibration curves. Of the 77 comparable compounds between the H₂ and He data, 80% (60 compounds) had similar or wider calibration ranges for H₂ and Hydrolnert results. H₂ carrier gas with the Hydrolnert source retains the sensitivity for most compounds when compared to the He data.

Response factor (RF) comparison

There is always concern about sensitivity and maintenance of response factors (RFs) for both single quadrupole and triple quadrupole systems when moving an analysis from He to H₂ carrier gas. Table 6 lists the RFs from EPA method 8270E guidance criteria (Table 4), RFs from a GC/MS analysis with He carrier gas, and RFs for GC/MS/MS analysis with the Hydrolnert source and H₂ carrier gas. All of these test systems used 9 mm extraction lenses, respective of the source type (e.g. the Hydrolnert source had a Hydrolnert 9 mm extraction lens). The RFs from EPA method 8270E Table 4 are guidance criteria and not requirements to pass the method, but ideally the RFs should be similar to these

guidance values. For the He GC/MS analysis, two compounds have RFs below the guidance criteria: hexachloroethane and N-nitroso-di-*n*-propylamine. For the H₂ Hydrolnert GC/MS/MS analysis, there were 14 more compounds with RF values lower than the guidance criteria than the He GC/MS system, but the GC/MS/MS also opens the potential to analyze lower concentration levels, down to 20 ng/mL, when the normal calibration range is 100 ng/mL to 100 µg/mL. Seven of these low RF compounds are within 0.2 counts of the suggested RF value. It is difficult to determine the significance of the difference, since the reference RF values are data generated on single quadrupole GC/MS systems using He carrier gas.

Repeatability in matrix

Table 6. RFs for select compounds (in alphabetical order) from EPA method 8270E (Table 4)⁴, GC/MS single quadrupole analysis with He carrier gas and GC/MS/MS triple quadrupole analysis with the Agilent Hydrolnert source and H₂ carrier gas.

Compound	RF from EPA 8270E ⁴	RF He GC/MS	RF H ₂ and Hydrolnert GC/MS/MS
Acenaphthene	0.9	1.3	0.2
Acenaphthylene	0.9	1.9	0.1
Acetophenone	0.01	1.2	1.0
Anthracene	0.7	1.1	0.9
Benzo(a)anthracene	0.8	1.4	1.0
Benzo(a)pyrene	0.7	1.2	1.0
Benzo(b)fluoranthene	0.7	1.4	1.2
Benzo(g,h,i)perylene	0.5	1.1	1.3
Benzo(k)fluoranthene	0.7	1.2	1.3
Bis(2-chloroethoxy)methane	0.3	0.4	0.7
Bis(2-chloroethyl)ether	0.7	0.8	0.5
Bis-(2-ethylhexyl)phthalate	0.01	0.8	0.2
4-Bromophenyl-phenyl ether	0.1	0.3	0.2
Butyl benzyl phthalate	0.01	0.6	0.1
4-Chloroaniline	0.01	0.4	0.6
4-Chloro-3-methylphenol	0.2	0.3	0.4
2-Chloronaphthalene	0.8	2.4	0.7
2-Chlorophenol	0.8	0.8	0.5
4-Chlorophenyl-phenyl ether	0.4	0.7	0.3
Chrysene	0.7	1.2	0.4
Dibenz(a,h)anthracene	0.4	1.1	0.2
Dibenzofuran	0.8	1.7	1.4
Di- <i>n</i> -butyl phthalate	0.01	1.3	0.5
3,3'-Dichlorobenzidine	0.01	0.5	0.1
2,4-Dichlorophenol	0.2	0.3	0.4
Diethyl phthalate	0.01	1.4	0.6
Dimethyl phthalate	0.01	1.4	0.8
2,4-Dimethylphenol	0.2	0.3	0.4
4,6-Dinitro-2-methylphenol	0.01	0.2	0.01
2,4-Dinitrophenol	0.01	0.2	0.01
2,4-Dinitrotoluene	0.2	0.4	0.02

Compound	RF from EPA 8270E ⁴	RF He GC/MS	RF H ₂ and Hydrolnert GC/MS/MS
2,6-Dinitrotoluene	0.2	0.3	0.03
Di- <i>n</i> -octyl phthalate	0.01	1.3	0.4
Fluoranthene	0.6	1.2	0.4
Fluorene	0.9	1.3	1.4
Hexachlorobenzene	0.1	0.3	0.4
Hexachlorobutadiene	0.01	0.2	0.4
Hexachlorocyclopentadiene	0.05	0.3	0.03
Hexachloroethane	0.3	0.2	0.1
Indeno(1,2,3-cd)pyrene	0.5	1.2	1.1
Isophorone	0.4	0.6	0.3
2-Methylnaphthalene	0.4	0.7	1.7
2-Methylphenol	0.7	0.7	0.6
4-Methylphenol	0.6	1.0	0.7
Naphthalene	0.7	1.1	0.9
2-Nitroaniline	0.01	0.4	0.05
3-Nitroaniline	0.01	0.3	0.02
4-Nitroaniline	0.01	0.3	0.1
Nitrobenzene	0.2	0.3	0.3
2-Nitrophenol	0.1	0.2	0.1
4-Nitrophenol	0.01	0.2	0.05
N-Nitroso-di- <i>n</i> -propylamine	0.5	0.4	0.03
N-Nitrosodiphenylamine	0.01	2.1	2.9
2,2'-Oxybis-(1-chloropropane)	0.01	0.5	0.03
Pentachlorophenol	0.05	0.2	0.1
Phenanthrene	0.7	1.2	1.1
Phenol	0.8	0.9	0.3
Pyrene	0.6	1.3	0.3
1,2,4,5-Tetrachlorobenzene	0.01	0.4	0.2
2,3,4,6-Tetrachlorophenol	0.01	0.4	0.07
2,4,5-Trichlorophenol	0.2	0.3	0.2
2,4,6-Trichlorophenol	0.2	0.3	0.2

The large EPA method 8270 mixture of compounds was also diluted to a concentration of 0.4 µg/mL to act as a calibration verification standard, since 0.4 µg/mL was not a specific calibration point. To test the repeatability of the HydroInert source in GC/MS/MS with H₂ carrier gas, the standard was sandwich-injected with 1 µL of a composite soil matrix to simulate a spiked matrix sample. This injection was repeated 10 times to understand the robustness of the method and to look for matrix enhancement, suppression, or potential contamination from the soil matrix. Table 7 contains the following data for each compound: calculated concentration of 0.4 µg/mL calibration verification in solvent, average concentration of the 10 replicates of 0.4 µg/mL calibration verification in soil matrix, the %RSD for the 10 replicate injections in soil matrix, and the recovery percentage comparing the soil matrix and solvent concentrations.

Compounds with calibration ranges that did not include 0.2 µg/mL or lower were not included in the table. For the 0.4 µg/mL solvent standard, only five compounds fell outside of the ±20% calibration verification window: sulfotep, dimethoate, diallate I, aramite I, and 7,12-dimethylbenz[a]anthracene. The first three compounds all were calibrated with quadratic fits and this verification concentration is low, which may be the reason for the high values. Normally, the calibration verification standard is closer to the midpoint of the calibration curve, but this study was pushing towards to lower limits with an on-column concentration of 0.02 µg/mL. Aramite I is just above the 20% limit at 0.481 µg/mL, while 7,12-dimethylbenz[a]anthracene is approximately half the

expected concentration at 0.22 µg/mL. All other compounds near 7,12-benz[a]anthracene are within the 20% limit, and it is unclear why this result is very low. For the replicate injections in soil, all but two compounds have a %RSD for the replicate injections below 10%, indicating the method is robust, even when running samples in matrix.

For the average concentrations in matrix, 17 compounds are outside the ±20% limit; 5 of these compounds are just above 0.48 µg/mL (less than 0.49 µg/mL), which may be minor signal enhancements from the matrix. Ten of these compounds are within 140% of the expected concentration of 0.4 µg/mL; furthermore, when the recovery percentage is calculated comparing the soil concentration to the solvent concentration, only six compounds fall outside of a ±20% recovery range, which again suggests signal enhancement. Bis(2-ethylhexyl) phthalate has a reported average concentration of 0.89 µg/mL, suggesting that there was bis(2-ethylhexyl) phthalate in the soil matrix. On the other hand, famphur appears to be suppressed by the matrix, as the average concentration in matrix was 0.272 µg/mL, but 0.402 µg/mL in solvent. In summary, for the soil matrix testing, we can easily detect the 0.4 µg/mL calibration verification standard consistently in matrix with over 85% of the compounds reporting inside the ±20% calibration range requirement. Typically, calibration verification is completed in solvent, where more than 95% of the compounds are inside the ±20% calibration range requirement.

Table 7. Comparison of the solvent-calculated concentration of the 0.4 µg/mL calibration verification standard, the average concentration (10 replicate injections) of the 0.4 µg/mL standard in soil matrix, the %RSD of the 10 replicate injections, and recovery percentage of the 0.4 µg/mL standard in matrix compared to solvent.

No.	Name	Calculated Concentration (0.4 µg/mL in Solvent)	Average Concentration in Matrix of 0.4 µg/mL Spike	%RSD of 10 Replicates	Recovery in matrix
1	NDMA	0.45	0.47	1.95%	104%
2	Pyridine	0.46	0.45	2.68%	97%
3	2-Picoline	0.45	0.45	2.54%	100%
4	N-Nitroso-N-methylethylamine	0.44	0.46	1.75%	106%
5	Methyl methanesulfonate	0.47	0.46	0.31%	99%
6	2-Fluorophenol	0.46	0.45	0.94%	99%
7	N-Nitroso-N-diethylamine	0.46	0.46	1.37%	100%
8	Ethyl methanesulfonate	0.45	0.45	0.68%	99%
9	Phenol-d ₆	0.46	0.45	0.67%	99%
10	Phenol	0.46	0.44	1.73%	96%
11	Aniline	0.46	0.46	1.51%	100%
12	bis(2-Chloroethyl)ether	0.46	0.45	0.87%	99%
13	2-Chlorophenol	0.44	0.45	1.28%	101%

No.	Name	Calculated Concentration (0.4 µg/mL in Solvent)	Average Concentration in Matrix of 0.4 µg/mL Spike	%RSD of 10 Replicates	Recovery in matrix
14	1,3-Dichlorobenzene	0.46	0.46	0.56%	100%
15	1,4-Dichlorobenzene	0.47	0.46	0.57%	98%
16	Benzyl alcohol	0.42	0.45	2.08%	108%
17	1,2-Dichlorobenzene	0.47	0.46	0.87%	99%
18	2-Methylphenol (o-cresol)	0.44	0.44	1.50%	99%
19	bis(2-Chloro-1-methylethyl)ether	0.47	0.46	4.86%	97%
20	N-Nitrosopyrrolidine	0.45	0.47	3.45%	103%
21	4-Methylphenol (p-Cresol)	0.40	0.42	1.65%	104%
22	Acetophenone	0.45	0.45	1.71%	100%
23	N-Nitrosodi-n-propylamine	0.42	0.43	5.84%	103%
24	4-Nitrosomorpholine	0.42	0.45	3.11%	107%
25	o-Toluidine	0.47	0.47	1.44%	99%
26	Hexachloroethane	0.44	0.48	2.32%	109%
27	Nitrobenzene-d ₅	0.43	0.49	2.66%	112%
28	Nitrobenzene	0.43	0.48	3.02%	110%
29	N-Nitrosopiperidine,	0.42	0.43	2.72%	104%
30	Isophorone	0.43	0.44	1.53%	103%
31	2-Nitrophenol	0.46	0.49	2.06%	106%
32	2,4-Dimethylphenol	0.43	0.43	1.30%	100%
33	bis(2-Chloroethoxy)methane	0.44	0.44	0.54%	101%
34	2,4-Dichlorophenol	0.40	0.43	0.92%	106%
35	1,2,4-Trichlorobenzene	0.46	0.46	0.56%	100%
37	Naphthalene	0.47	0.46	0.66%	98%
38	4-Chloroaniline	0.45	0.46	1.13%	102%
39	2,6-Dichlorophenol	0.41	0.44	1.32%	106%
40	Hexachlorobutadiene	0.46	0.46	0.52%	100%
41	p-Phenylenediamine	0.45	0.44	3.75%	97%
42	N-Nitrosodi-n-butylamine	0.42	0.44	1.67%	104%
43	4-Chloro-3-methylphenol	0.43	0.43	1.45%	101%
44	2-Methylnaphthalene	0.47	0.47	0.60%	99%
45	Hexachlorocyclopentadiene	0.41	0.40	3.72%	96%
46	1,2,4,5-Tetrachlorobenzene	0.47	0.47	1.39%	99%
47	2,4,6-Trichlorophenol	0.42	0.43	1.47%	103%
48	2,4,5-Trichlorophenol	0.41	0.39	4.58%	97%
49	2-Fluorobiphenyl	0.47	0.46	0.74%	99%
50	1-Chloronaphthalene	0.47	0.46	0.78%	98%
51	2-Chloronaphthalene	0.47	0.46	1.55%	98%
52	2-Nitroaniline	0.44	0.53	0.90%	120%
53	Dimethyl phthalate	0.42	0.44	0.92%	106%
54	2,6-Dinitrotoluene	0.44	0.47	2.90%	106%
55	Acenaphthylene	0.44	0.43	2.28%	99%
56	m-Nitroaniline	0.39	0.43	4.35%	112%
57	Acenaphthene	0.48	0.46	1.14%	95%
59	Pentachlorobenzene	0.46	0.45	1.85%	98%
60	4-Nitrophenol	0.37	0.44	3.35%	120%

No.	Name	Calculated Concentration (0.4 µg/mL in Solvent)	Average Concentration in Matrix of 0.4 µg/mL Spike	%RSD of 10 Replicates	Recovery in matrix
61	Dibenzofuran	0.47	0.46	0.58%	99%
62	2,4-Dinitrotoluene	0.42	0.44	3.98%	105%
63	1-Naphthylamine	0.37	0.47	1.19%	126%
64	2,3,4,6-Tetrachlorophenol	0.40	0.42	1.79%	106%
65	2-Naphthylamine	0.40	0.44	1.66%	110%
66	Diethyl phthalate	0.41	0.45	1.02%	111%
67	Fluorene	0.47	0.47	0.82%	101%
68	Thionazin	0.42	0.46	2.38%	109%
69	5-Nitro- <i>o</i> -toluidine	0.40	0.45	8.22%	114%
70	4-Chlorophenyl phenyl ether	0.48	0.46	1.00%	96%
71	4-Nitroaniline	0.43	0.38	7.92%	88%
72	2-Methyl-4,6-dinitrophenol (DNOC)	0.46	0.52	5.22%	112%
73	N-Nitrosodiphenylamine	0.46	0.46	0.97%	101%
74	Diphenylamine	0.45	0.47	0.94%	104%
75	Azobenzene	0.47	0.50	2.62%	107%
76	2,4,6-Tribromophenol	0.42	0.43	3.11%	104%
77	Sulfotep	0.53	0.52	4.03%	97%
78	Dimethoate	0.64	0.52	12.70%	81%
79	Diallate I	2.70	0.53	2.91%	102%
80	Phorate	0.47	0.53	2.47%	111%
81	Phenacetin	0.42	0.44	1.40%	105%
82	4-Bromophenyl phenyl ether	0.45	0.44	2.94%	98%
83	Hexachlorobenzene	0.46	0.46	1.43%	100%
85	Pentachloronitrobenzene	0.41	0.46	3.62%	111%
86	4-Aminobiphenyl	0.44	0.45	1.56%	103%
87	Propyzamide	0.40	0.43	1.92%	107%
88	Phenanthrene	0.48	0.48	0.67%	101%
89	Dinoseb	0.42	0.43	3.59%	103%
90	Disulfoton	0.43	0.48	2.15%	111%
91	Anthracene	0.44	0.46	1.26%	104%
92	Parathion-methyl	0.42	0.40	1.25%	94%
93	Di- <i>n</i> -butyl phthalate	0.38	0.41	1.25%	106%
94	4-Nitroquinoline-1-oxide	0.42	0.41	11.49%	97%
95	Parathion	0.41	0.45	2.50%	112%
96	Fluoranthene	0.47	0.47	0.79%	100%
97	Benzidine	0.42	0.45	7.96%	105%
98	Pyrene	0.47	0.48	0.38%	101%
99	<i>p</i> -Terphenyl- <i>d</i> ₁₄	0.46	0.46	0.82%	101%
100	Aramite I	0.48	0.51	2.28%	106%
101	Aramite II	0.48	0.50	2.85%	105%
102	<i>p</i> -(Dimethylamino)azobenzene	0.47	0.51	2.10%	108%
103	Chlorobenzilate	0.41	0.45	1.07%	108%
104	Famphur	0.40	0.27	3.75%	68%
105	3,3'-Dimethylbenzidine	0.46	0.47	2.96%	101%
106	Butyl benzyl phthalate	0.40	0.43	1.32%	109%

No.	Name	Calculated Concentration (0.4 µg/mL in Solvent)	Average Concentration in Matrix of 0.4 µg/mL Spike	%RSD of 10 Replicates	Recovery in matrix
107	Benz[a]anthracene	0.44	0.45	0.31%	101%
108	3,3'-Dichlorobenzidine	0.41	0.43	2.23%	105%
109	Chrysene	0.47	0.47	0.62%	99%
110	bis(2-Ethylhexyl) phthalate	0.44	0.89	1.80%	205%
111	Di- <i>n</i> -octyl phthalate	0.43	0.45	1.37%	104%
112	Benzo[b]fluoranthene	0.44	0.46	1.25%	105%
113	7,12-Dimethylbenz[a]anthracene	0.22	0.40	1.83%	182%
114	Benzo[k]fluoranthene	0.46	0.43	2.74%	94%
115	Benzo[a]pyrene	0.41	0.42	2.09%	103%
116	3-Methylcholanthrene	0.40	0.41	1.34%	104%
117	Dibenz[a,j]acridine	0.44	0.46	1.56%	104%
118	Indeno[1,2,3-cd]pyrene	0.41	0.42	1.01%	104%
119	Dibenz[a,h]anthracene	0.43	0.44	3.11%	103%
120	Benzo[g,h,i]perylene	0.43	0.44	1.87%	104%

Conclusion

Due to the high sensitivity achieved with MRM mode and the inertness of the Agilent HydroInert source with H₂ carrier gas, 92.5% of the 120 tested compounds were detected and calibrated in the normal calibration range for EPA method 8270E from 0.1 to 100 µg/mL, and 77 compounds reached the extended calibration range of 0.02 to 100 µg/mL. Additionally, only 16 compounds required curve fits to pass EPA Method 8270E calibration criteria. Method criteria for EPA method 8270E were met for initial calibration over a working range of 0.02 to 100 µg/mL in a single 12-minute run using H₂ carrier gas and the HydroInert source, while retaining mass spectral fidelity and existing MRM transitions for compounds susceptible to H₂ reactivity.

References

1. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method 8270D. *United States Environmental Protection Agency*, Revision 4, February **2007**.
2. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method 8270E. *United States Environmental Protection Agency*, Revision 4, June **2018**.
3. Churley, M.; Quimby, B.; Andrianova, A. A Fast Method for EPA 8270 in MRM Mode Using the 7000 Series Triple Quadrupole GC/MS, *Agilent Technologies application note*, publication number 5994-0691EN, **2019**.

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DE73549906

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 Printed in the USA, May 27, 2022
 5994-4891EN