

Analysis of Semivolatile Organic Compounds Using Hydrogen Carrier Gas and the Agilent HydroInert Source by Gas Chromatography/Mass Spectrometry

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Abstract

Gas chromatography/mass spectrometry (GC/MS) is integral to the analysis of semivolatile organic compounds (SVOCs) in environmental matrices. Recent pressure on the helium (He) supply has required organizations to actively investigate hydrogen (H₂) carrier gas, but most GC/MS analyses have reduced sensitivity and hydrogenation or dechlorination in the sources. The Agilent HydroInert source retains the ability to analyze a wide calibration range (0.1 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 is regarded as the select analytical technique for the analysis of SVOCs. Governmental regulatory authorities have established methods and performance criteria for the measurement of SVOCs identified as pollutants in environmental and industrial matrices. For example, the U.S. EPA method 8270 (versions 8270D and 8270E) contains a list of over 200 compounds suitable for analysis by GC/MS in solid waste, soil, air, and water extracts.^{1,2} Method 8270 contains SVOCs across several analyte class types from acids, bases, neutral compounds, and polyaromatic hydrocarbons (PAHs); this method also has detailed specifications and requirements for the Quantitative Analysis of SVOCs.

The availability of helium (He) has been a concern for several years, but interest in transitioning to alternative carrier gases, such as hydrogen (H₂) has significantly increased in recent years. However, existing MS systems have issues with hydrogenation of some functional groups, such as nitro compounds, or dechlorination of heavily chlorinated compounds; these issues would alter the mass spectra of a peak in the total ion chromatogram (TIC) and lead to potential misidentification of compounds. A newly designed extractor source for the Agilent 5977B Inert Plus GC/MSD addresses these H₂-related issues and helps improve performance with H₂ carrier gas in GC/MS. The Hydrolnert source with H₂ carrier gas retains mass spectral fidelity and can allow users to continue to use existing He-based mass spectral libraries and quantitative methods.

This application note demonstrates the ability of the Hydrolnert 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. Also, a method for EPA 8270 has been developed that retains similar sensitivity to a He carrier gas analysis, which allows for most compounds to be calibrated between 0.1 to 100 µg/mL with fewer than 20% of compounds requiring linear curve fits.

Experimental

A set of stock standards containing 119 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 (part number ISM-560) 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: 0.1, 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 the retention order of the targets and surrogates, with the internal standards listed at the end of the table out of the 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 25 µg/mL and used to obtain the MS calibration and tuning settings.

A composite mixture of soils extracted with dichloromethane was prepared for EPA method 8270 analysis. The mixture was 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	43	4-Chloro-3-methylphenol	85	Pentachlorophenol
2	Pyridine	44	2-Methylnaphthalene	86	Pentachloronitrobenzene
3	2-picoline	45	Hexachlorocyclopentadiene	87	Propyzamide
4	N-Nitroso-N-methylethylamine	46	1,2,4,5-Tetrachlorobenzene	88	Dinoseb
5	Methyl methanesulfonate	47	2,4,6-Trichlorophenol	89	Disulfoton
6	2-Fluorophenol	48	2,4,5-Trichlorophenol	90	Phenanthrene
7	N-Nitrosodiethylamine	49	2-Fluorobiphenyl (surrogate)	91	Anthracene
8	Ethyl methanesulfonate	50	2-Chloronaphthalene	92	Methyl parathion
9	Phenol-d ₆ (surrogate)	51	1-Chloronaphthalene	93	Dibutyl phthalate
10	Phenol	52	2-Nitroaniline	94	Parathion
11	Aniline	53	Dimethyl phthalate	95	4-Nitroquinoline-1-oxide
12	Bis(2-chloroethyl) ether	54	2,6-Dinitrotoluene	96	Fluoranthene
13	2-Chlorophenol	55	Acenaphthylene	97	Benzidine
14	1,3-Dichlorobenzene	56	<i>m</i> -Nitroaniline	98	Pyrene
15	1,4-Dichlorobenzene	57	Acenaphthene	99	Aramite
16	Benzyl alcohol	58	2,4-Dinitrophenol	100	<i>p</i> -Terphenyl-d ₁₄ (surrogate)
17	1,2-Dichlorobenzene	59	4-Nitrophenol	101	Aramite II
18	2-Methylphenol (<i>o</i> -cresol)	60	Pentachlorobenzene	102	<i>p</i> -(Dimethylamino)azobenzene
19	Bis(2-chloro-1-methylethyl) ether	61	2,4-Dinitrotoluene	103	Chlorobenzilate
20	1-Nitrosopyrrolidine	62	Dibenzofuran	104	3,3'-Dimethylbenzidine
21	<i>p</i> -Cresol	63	1-Naphthalenamine	105	Benzyl butyl phthalate
22	N-Nitrosodi- <i>n</i> -propylamine	64	2,3,4,6-Tetrachlorophenol	106	3,3'-Dichlorobenzidine
23	Acetophenone	65	2-Naphthalenamine	107	Benz[a]anthracene
24	4-Nitrosomorpholine	66	Diethyl phthalate	108	Chrysene
25	<i>o</i> -Toluidine	67	Thionazin	109	Bis(2-ethylhexyl) phthalate
26	Hexachloroethane	68	Fluorene	110	Di- <i>n</i> -octyl phthalate
27	Nitrobenzene-d ₅ (surrogate)	69	4-Chlorophenyl phenyl ether	111	7,12-Dimethylbenz[a]anthracene
28	Nitrobenzene	70	5-Nitro- <i>o</i> -toluidine	112	Benzo[b]fluoranthene
29	N-Nitrosopiperidine	71	4-Nitroaniline	113	Benzo[k]fluoranthene
30	Isophorone	72	2-Methyl, 4,6-dinitrophenol	114	Benzo[a]pyrene
31	2-Nitrophenol	73	Diphenylamine	115	3-Methylcholanthrene
32	2,4-Dimethylphenol	74	Azobenzene	116	Dibenz[a,j]acridine
33	Benzoic acid	75	2,4,6-Tribromophenol	117	Indeno(1,2,3- <i>cd</i>)pyrene
34	Bis(2-chloroethoxy)methane	76	Sulfotep	118	Dibenz[a,h]anthracene
35	2,4-Dichlorophenol	77	Diallate I	119	Benzo[ghi]perylene
36	1,2,4-Trichlorobenzene	78	Diallate II	120	1,4-Dichlorobenzene-d ₄ (internal standard)
37	Naphthalene	79	Phorate	121	Naphthalene-d ₈ (internal standard)
38	<i>a,a</i> -Dimethylphenethylamine	80	Phenacetin	122	Acenaphthalene-d ₁₀ (internal standard)
39	<i>p</i> -Chloroaniline	81	4-Bromophenyl phenyl ether	123	Phenanthrene-d ₁₀ (internal standard)
40	2,6-Dichlorophenol	82	Hexachlorobenzene	124	Chrysene-d ₁₂ (internal standard)
41	Hexachlorobutadiene	83	Dimethoate	125	Perylene-d ₁₂ (internal standard)
42	N-nitrosodibutylamine	84	4-Aminobiphenyl		

Instrumental methods

The Agilent 8890 GC system was configured with an Agilent J&W DB-5ms Ultra Inert column (part number 121-5523UI) interfaced with an Agilent 5977B Inert Plus MS system with an Agilent HydroInert source. Table 2 summarizes the GC/MS instrumentation and consumables used in this study. The GC and MSD 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 method 8270 guidelines for method parameters, such as scan range and scan rate.

Instrumentation

Table 2. GC and MSD instrumentation and consumables.

Parameter	Value
GC	Agilent 8890 GC system
MS	Agilent 5977B Inert Plus GC/MSD
Source	Agilent HydroInert source with 9 mm HydroInert extraction lens
Syringe	Agilent Blue Line autosampler syringe, 10 μ L, PTFE-tip plunger (part number G4513-80203)
Column	Agilent DB-5ms Ultra Inert, 20 m \times 0.18 mm, 0.36 μ m (part number 121-5523UI)
Inlet Liner	Agilent Ultra Inert inlet liner, split, low pressure drop, glass wool (part number 5190-2295)

Instrument conditions

Table 3. GC and MSD instrument conditions.

Parameter	Value
Injection Volume	1 μ L
Inlet	230 °C Split 10:1
Column Temperature Program	40 °C (0 min hold) 30 °C/min to 320 °C (hold 2 min)
Carrier Gas and Flow Rate	H ₂ , 1.2 mL/min constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	300 °C
Quadrupole Temperature	150 °C
Scan	35 to 500 <i>m/z</i>
Tune	etune.u
Gain Factor	0.5
Threshold	0
A/D Samples	4

Method development

Switching carrier gas from He to H₂ introduced several challenges for EPA method 8270 analyses with a GC/MS single quadrupole instrument. Balance between sensitivity changes, inlet pressure and flow rates, and column capacity and dimensions must be managed to attain the required calibration range of 0.1 to 100 μ g/mL for most compounds. For example, if the typical EPA method 8270 analysis with He carrier gas used a 30 m \times 0.25 mm, 0.25 μ m DB-5ms Ultra Inert column was changed to use a 20 m \times 0.18 mm, 0.18 μ m DB-5ms Ultra Inert column for H₂ carrier gas, this 20 m column would have ~33% of the 30 m column capacity, requiring changes to the injection parameters to avoid column overload. However, when a 20:1 split injection was used, limitations in sensitivity were observed with issues of reaching below 0.5 μ g/mL injected concentration (25 ng/mL on column); using etune.u did not solve the issue. Another investigated method used the 30 m \times 0.25 mm, 0.25 μ m DB-5ms Ultra Inert column with a pulsed splitless injection and 1.5 mL/min flow rate. This method could reach the 0.1 μ g/mL lower-end concentration for most compounds but had issue with severely fronting peaks above ~75 μ g/mL, indicating overload, which also caused an increase in linear fits. A pulsed split injection with 10:1 split was tested for the 30 m column method with an atune.u tune, but most compounds were not detected at 0.1 μ g/mL. For the column referenced in this work (20 m \times 0.18 mm, 0.36 μ m DB-5ms Ultra Inert), various injection parameters and both atune and etune algorithms were tested. The final method parameters listed in Table 3 provided the best balance between column capacity, sensitivity, and ability to produce calibration results in the 0.1 to 100 μ g/mL range. While atune would be preferred, the lowest concentration tended to end at 0.2 μ g/mL for most of the compounds.

Results and discussion

Mass spectral fidelity

A major concern with H₂ carrier gas is changes in the mass spectra of nitro compounds and heavily halogenated compounds. In the presence of H₂, high temperature, and metal surfaces, nitro functional groups are hydrogenated to amines, while heavily chlorinated compounds are dechlorinated; all these factors are present in the mass spectrometer. The following is an example of the benefits of the Hydrolnert source with nitrobenzene. In an experiment with an extractor source with a 3 mm extraction lens, H₂ was used as the carrier gas, where nitrobenzene was one of the compounds in the mixture (part number SVM-122-1). Hydrogenation of nitrobenzene (molecular weight (MW) 123 *m/z*) will form aniline (MW 93 *m/z*). When reviewing the mass spectrum under the TIC peak for the extractor source and H₂ carrier gas, the mass spectrum in Figure 1A was observed. There is a large abundance of 93 *m/z* and low 123 *m/z*, indicating conversion of nitrobenzene to aniline in the source; this is confirmed to occur in the source because the mass spectrum is observed at the retention time of nitrobenzene, which is well separated from aniline. Comparatively, the same mixture containing nitrobenzene was tested on a Hydrolnert source (with a 9 mm extraction lens), where we observe the expected distribution of 123 and 93 *m/z* in the mass spectrum (Figure 1B), indicating that the nitrobenzene is retained in the source and not converted to aniline. This comparison can also be reviewed in the extracted ion chromatograms (EICs) shown in Figure 2A (for the extractor source conversion) and 2B (for Hydrolnert source retention of nitrobenzene), where there is an improved 123/93 ratio using the Hydrolnert source, while the extractor source EIC overlay shows significant conversion to 93 *m/z* and significant tailing.

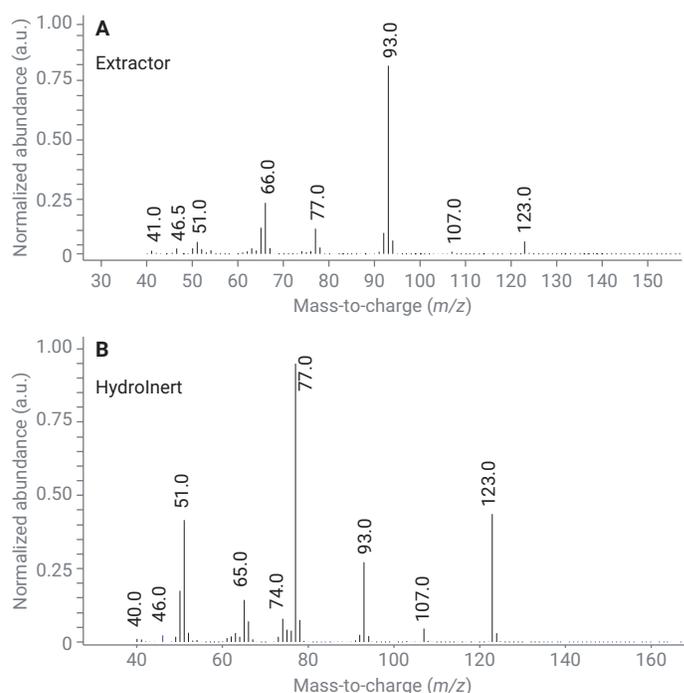


Figure 1. Mass spectra for peak eluting at nitrobenzene retention time with H₂ carrier gas in (A) extractor source with 3 mm extraction lens showing hydrogenation to aniline with the abundant 93 *m/z* ion and (B) Agilent Hydrolnert source, showing an improved mass spectrum that correlates to nitrobenzene.

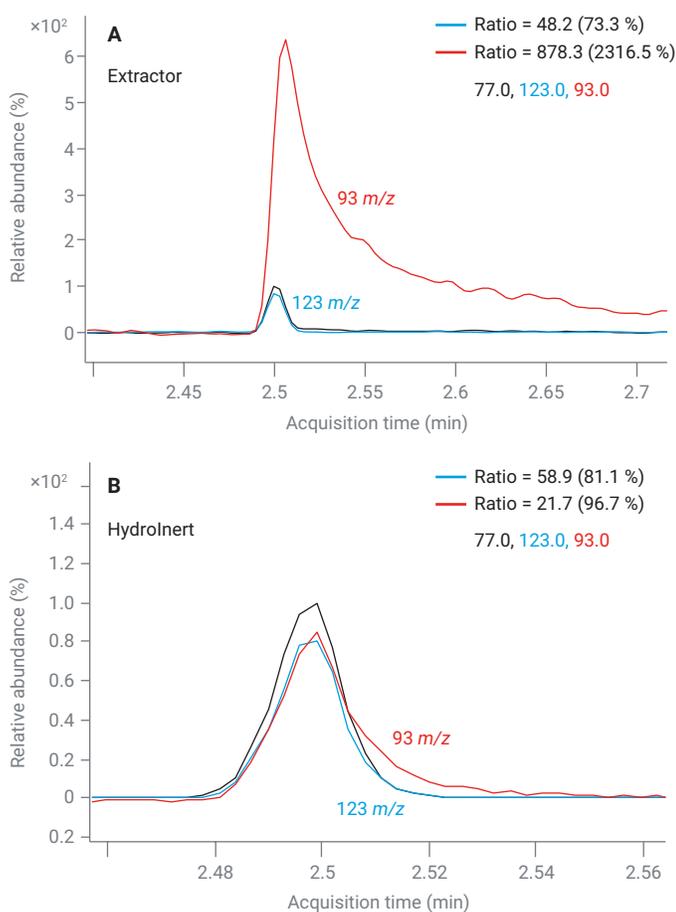


Figure 2. EICs of nitrobenzene with H₂ carrier gas in (A) extractor source with 3 mm extraction lens showing hydrogenation to aniline with the abundant 93 m/z ion and (B) Agilent HydroInert source, showing an improved 123 versus 93 m/z ratio.

GC/MS tuning mix

A critical component of EPA method 8270 is the tune criteria associated with the ion ratios of DFTPP. This method used the etune algorithm for the factor of 10 increase in signal to balance the split injection. For the GC/MS single quadrupole system, the DFTPP ion ratio criteria from Table 3 of EPA methods 8270E and 8270D were used to test the HydroInert source with H₂ carrier gas.^{1,2} The EPA method 8270D includes more ion ratio criteria than EPA 8270E, which reflects the EPA 525 criteria table. 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 both the EPA method 8270E and 8270D ion ratio criteria.

Table 4. DFTPP ions, abundance criteria from EPA method 8270D and 8270E^{1,2}, measured relative abundance, and pass/fail of the relative abundance.

Target Mass (m/z)	Ion Abundance Criteria	Measured Relative Abundance	Pass/Fail
51	*10 to 80% of 198 m/z	38.5%	Pass
68	<2% of 69 m/z	1.0%	Pass
69	Present	36.5%	Pass
70	<2% of 69 m/z	0.4%	Pass
127	*10 to 80% of 198 m/z	54.4%	Pass
197	<2% of 198 m/z	0.0%	Pass
198	Base peak or present *or >50% of 442 m/z	51.6%	Pass
199	5 to 9% of 198 m/z	5.0%	Pass
275	10 to 60% of base peak	30.4%	Pass
365	>1% of base peak	4.9%	Pass
441	<150% of 443 m/z present, *but <24% of 442	83.1%, *15.7%	Pass
442	Base peak or present *or >50% of 198 m/z	100% (base peak)	Pass
443	15 to 24% of 442 m/z	18.9%	Pass

* Denotes 8270D requirement difference from EPA method 8270E requirement.

There is always concern for 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 or use a temperature-programmable inlet, such as the multimode inlet to protect the active compounds, while still being able to increase the temperature to 320 °C and drive out the PAHs. This study used the most common inlet existing in laboratories, the split/splitless inlet, and ran the inlet at 230 °C.

Reviewing the results of the GC/MS tuning mixture for DDT breakdown and compound tailing factors, the DDT (%) breakdown was 0.2%, the pentachlorophenol tailing factor was 1.2, and the benzidine tailing factor was 1.3. All values are within the EPA method 8270 criteria of <20% DDT breakdown and tailing factors <2.0.

Calibration criteria

The initial calibration consisted of 13 levels across the concentration range of 0.1 to 100 µg/mL for this 12-minute method. Figure 3 is a TIC of the target analytes, surrogates, and internal standards.

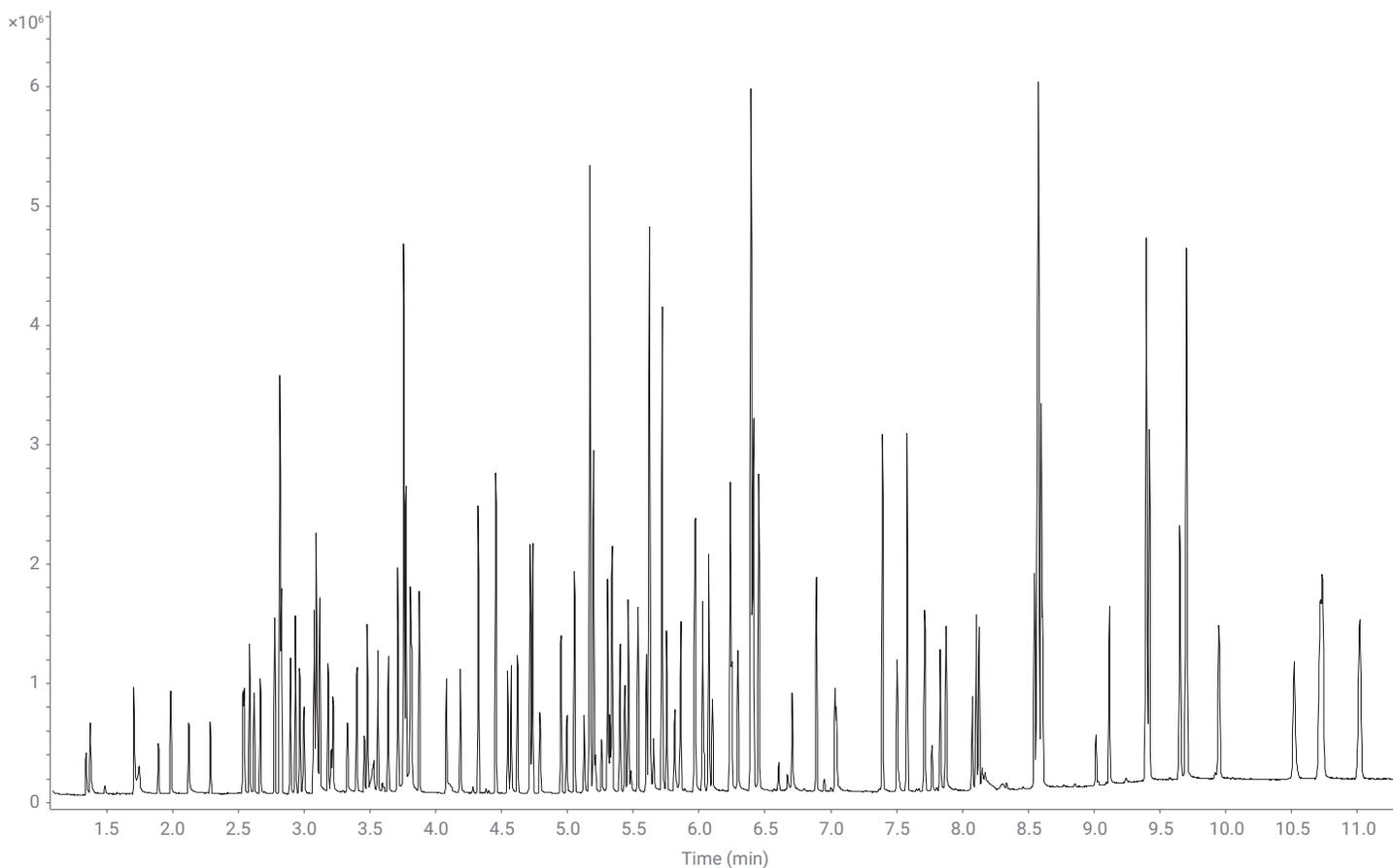


Figure 3. TIC of the 20 µg/mL calibration standard containing 119 target analytes and surrogates and six internal standards using H₂ carrier gas and the Agilent HydroInert source.

Critical pair resolution

With the shorter method time and a different column, critical pair resolution above 50% was verified for phenanthrene and anthracene (EIC 178 *m/z*), benz[a]anthracene and chrysene (EIC 228 *m/z*), and benzo(b)fluoranthene and benzo(k)fluoranthene (EIC 252 *m/z*). All three isomer pairs are

shown in Figure 4 at a midlevel concentration of 5 µg/mL; phenanthrene and anthracene (Figure 4A) have baseline resolution, benz[a]anthracene and chrysene (Figure 4B) are nearly baseline-resolved, and benzo(b)fluoranthene and benzo(k)fluoranthene (Figure 4C) are over 50% resolved, satisfying the EPA method 8270 criteria.

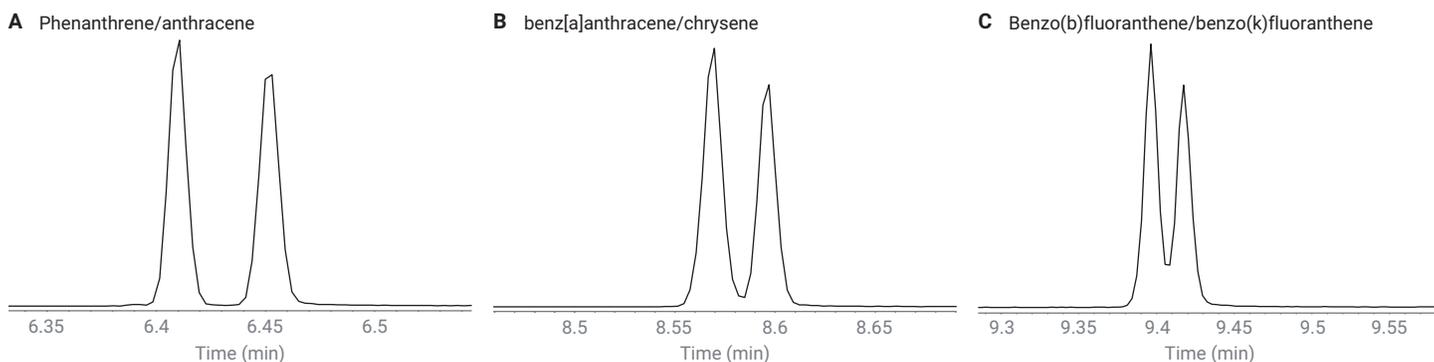


Figure 4. Midlevel standard (5 µg/mL) EICs for critical isomer pairs: (A) phenanthrene and anthracene (EIC 178 *m/z*); (B) benz[a]anthracene and chrysene (EIC 228 *m/z*); (C) benzo(b)fluoranthene and benzo(k)fluoranthene (EIC 252 *m/z*).

Response factor comparison between hydrogen and helium carrier gases

When moving an analysis from He to H₂ carrier gas, there is always concern about maintenance of response factors (RFs) and sensitivity for single quadrupole systems. Table 5 lists the RFs from EPA method 8270E guidance criteria (Table 4); RFs from a GC/MS analysis with He carrier gas when using a splitless injection, then a pulsed split injection, and RFs for GC/MS analysis with the HydroInert source and H₂ carrier gas. Since the H₂ method uses a split injection, the pulsed split injection with He provides a good comparison, while the splitless He data is the traditional analysis. The RFs from EPA method 8270E (Table 4) are guidance criteria and not requirements to pass the method, but ideally the RFs should be like these guidance values. For the He (splitless injection) GC/MS analysis, two compounds have RFs below the guidance criteria: hexachloroethane and N-nitroso-di-*n*-propylamine; these compounds' RFs are also low for the H₂ HydroInert results. For the H₂ HydroInert GC/MS analysis, five additional compounds have RFs below the guidance criteria, where four are within 0.1 points. For example, the guidance RF criteria for bis(2-chloroethyl)ether is 0.7 and the H₂ HydroInert GC/MS RF was 0.6. For the pulsed split He GC/MS results, all reported RFs match or are higher than the guidance from the EPA, but this data set did not report RFs for the seven indicated compounds in Table 5. In total, only seven compounds of the 72 listed in Table 5 had RFs lower than the EPA guidance for the H₂ HydroInert GC/MS results; five of these were within 0.1 points of the guidance RF value, and the other two RF values were within 0.3 or fewer points of the guidance.

Table 5. RFs for select compounds from EPA method 8270E (Table 4 in the EPA method)², GC/MS single quadrupole analysis with He carrier gas³, GC/MS single quadrupole analysis with He and pulsed split injection⁴, and GC/MS single quadrupole analysis with the Agilent HydroInert source and H₂ carrier gas.

Compound	Response Factors			
	From EPA 8270E	He GC/MS ³	He GC/MS, Pulsed Split ⁴	H ₂ HydroInert GC/MS
Acenaphthene	0.9	1.3	1.1	1.1
Acenaphthylene	0.9	1.9	2.0	1.4
Acetophenone	0.01	1.2	--	0.4
Anthracene	0.7	1.1	1.1	1.0
Benzo(a)anthracene	0.8	1.4	1.3	1.5
Benzo(a)pyrene	0.7	1.2	1.0	0.9
Benzo(b)fluoranthene	0.7	1.4	1.0	1.2
Benzo(g,h,i)perylene	0.5	1.1	1.1	1.0
Benzo(k)fluoranthene	0.7	1.2	1.1	1.2
Bis(2-chloroethoxy)methane	0.3	0.4	0.4	0.3
Bis(2-chloroethyl)ether	0.7	0.8	1.1	0.6
Bis-(2-ethylhexyl)phthalate	0.01	0.8	0.5	0.5
4-Bromophenyl-phenyl ether	0.1	0.3	0.2	0.2
Butyl benzyl phthalate	0.01	0.6	0.5	0.3
4-Chloroaniline	0.01	0.4	0.4	0.4
4-Chloro-3-methylphenol	0.2	0.3	0.2	0.2
2-Chloronaphthalene	0.8	2.4	1.2	1.0
2-Chlorophenol	0.8	0.8	1.2	0.7
4-Chlorophenyl-phenyl ether	0.4	0.7	0.6	0.5
Chrysene	0.7	1.2	1.2	1.1
Dibenz(a,h)anthracene	0.4	1.1	1.0	1.0
Dibenzofuran	0.8	1.7	1.7	1.5
Di- <i>n</i> -butyl phthalate	0.01	1.3	1.2	0.8
3,3'-Dichlorobenzidine	0.01	0.5	--	0.4
2,4-Dichlorophenol	0.2	0.3	0.3	0.2
Diethyl phthalate	0.01	1.4	1.3	1.0
Dimethyl phthalate	0.01	1.4	1.3	1.0
2,4-Dimethylphenol	0.2	0.3	0.3	0.3
4,6-Dinitro-2-methylphenol	0.01	0.2	--	0.1
2,4-Dinitrophenol	0.01	0.2	--	0.1
2,4-Dinitrotoluene	0.2	0.4	0.3	0.2
2,6-Dinitrotoluene	0.2	0.3	0.3	0.2
Di- <i>n</i> -octyl phthalate	0.01	1.3	1.4	0.8
Fluoranthene	0.6	1.2	1.2	1.2
Fluorene	0.9	1.3	1.3	1.2
Hexachlorobenzene	0.1	0.3	0.3	0.3
Hexachlorobutadiene	0.01	0.2	0.2	0.2
Hexachlorocyclopentadiene	0.05	0.3	0.4	0.1
Hexachloroethane	0.3	0.2	0.5	0.1
Indeno(1,2,3-cd)pyrene	0.5	1.2	1.0	1.2
Isophorone	0.4	0.6	0.5	0.4

Compound	Response Factors			
	From EPA 8270E	He GC/MS ³	He GC/MS, Pulsed Split ⁴	H ₂ Hydrolnert GC/MS
2-Methylnaphthalene	0.4	0.7	0.7	0.7
2-Methylphenol	0.7	0.7	1.0	0.6
4-Methylphenol	0.6	1.0	1.1	0.3
Naphthalene	0.7	1.1	1.0	1.0
2-Nitroaniline	0.01	0.4	0.3	0.2
3-Nitroaniline	0.01	0.3	0.3	0.2
4-Nitroaniline	0.01	0.3	0.3	0.2
Nitrobenzene	0.2	0.3	0.3	0.2
2-Nitrophenol	0.1	0.2	0.2	0.1
4-Nitrophenol	0.01	0.2	--	0.1
N-Nitroso-di-n-propylamine	0.5	0.4	0.7	0.4
N-Nitrosodiphenylamine	0.01	2.1	0.6	0.9
2,2'-Oxybis-(1-chloropropane)	0.01	0.5	1.1	0.5
Pentachlorophenol	0.05	0.2	--	0.1
Phenanthrene	0.7	1.2	1.1	1.1
Phenol	0.8	0.9	1.4	0.7
Pyrene	0.6	1.3	1.3	1.2
1,2,4,5-Tetrachlorobenzene	0.01	0.4	--	0.3
2,3,4,6-Tetrachlorophenol	0.01	0.4	0.3	0.2
2,4,5-Trichlorophenol	0.2	0.3	0.4	0.3
2,4,6-Trichlorophenol	0.2	0.3	0.4	0.2

Calibration results

A multipoint calibration was performed with the maximum of 13 concentration levels and the relative RF was determined for each compound and calibration level. The mean RF was calculated to build the calibration curve of each compound along with the relative standard deviation (RSD). The average RF %RSD must be <20%, which is the preferred passing criteria; if not achievable with at least six calibration levels, an R² value >0.990 is required for a linear curve fit, or a quadratic fit may be used. Accuracy for the lowest data point must be within 30% of estimated concentration with a minimum of six points for the curve fit. Results for the initial calibration using H₂ carrier gas and the Hydrolnert source can be found in Table 6.

Of 119 compounds, 14 compounds required linear fits and one quadratic fit was required. Table 6 summarizes the calibration results for the 119 target compounds and surrogates with average RF %RSD values, and the lowest and highest concentration level if the values are different from the full calibration range (0.1 to 100 µg/mL). Over 87% of the compounds pass the calibration criteria with an average RF %RSD below 20%. An increase in the number of compounds requiring linear fits is predictable since H₂ is more reactive than He and the inlet is set to a lower temperature to avoid formation of hydrochloric acid in the presence of higher temperatures and water in the inlet. Use of a multimode inlet may result in improved heavy phthalate and PAH results.

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, 96 compounds were analyzed in a previous application for EPA method 8270 with He carrier gas on GC/MS.³ Comparing these compounds with the same set using the Hydrolnert source and H₂ carrier gas (also GC/MS), 15 compounds have a narrower calibration range, where six compounds are only narrower by one concentration level starting at 200 ng/mL instead of 100 ng/mL, and four compounds start at 500 ng/mL. For benzoic acid, the Hydrolnert source with H₂ carrier as has the same calibration range of 0.8 to 100 µg/mL, as observed with He carrier gas on a GC/MS; 2,4-dinitrophenol passed calibration criteria with average RF for the range of 0.5 to 100 µg/mL with H₂ and the Hydrolnert source, while helium-collected data required a linear fit for the same calibration range. Pentachlorophenol also had matched calibration ranges between the He and H₂ results of 0.5 to 100 µg/mL, but the H₂ data required a linear fit. On the positive side, some compounds had wider calibration ranges with H₂ and the Hydrolnert source, such as 4-nitrophenol and 2-methyl-4,6-dinitrophenol, which each included an extra calibration level of 100 and 200 ng/mL, respectively. Also, these two compounds did not require linear curve fits, but passed calibration criteria with average RF %RSD values of 18.7% for 4-nitrophenol and 19.7% for 2-methyl-4,6 dinitrophenol. In total, 24 compounds out of 119 had narrower calibration ranges than the default of 0.1 to 100 µg/mL. The use of H₂ carrier gas with the Hydrolnert source retains the sensitivity range for over 84% of the previously tested 96 SVOCs.

Table 6. Initial calibration results for 119 target compounds and surrogates for H₂ carrier gas and the Agilent HydroInert source for EPA method 8270.

Name	Retention Time (min)	Average RF	Average RF %RSD	Curve Fit R ²	Curve Fit	Low Standard (µg/mL)	High Standard (µg/mL)
						Default is 0.1 to 100 µg/mL	
N-Nitrosodimethylamine	1.339	0.273	7.41				
Pyridine	1.372	0.459	15.39			0.5	
2-Picoline	1.705	0.561	5.89				
N-Nitroso-N-methylethylamine	1.741	0.232	7.23				
Methyl methanesulfonate	1.890	0.256	15.04				
2-Fluorophenol	1.983	0.568	5.20				
N-Nitroso-N-diethylamine	2.120	0.258	7.13				
Ethyl methanesulfonate	2.286	0.374	13.02				
Phenol-d ₆	2.532	0.667	4.93				
Phenol	2.541	0.664	6.32				
Aniline	2.583	0.968	7.50				
Bis(2-chloroethyl) ether	2.617	0.616	10.72				
2-Chlorophenol	2.665	0.661	8.50				
1,3-Dichlorobenzene	2.774	0.773	6.96				
1,4-Dichlorobenzene	2.825	0.804	7.53				
Benzyl alcohol	2.892	0.442	12.90				
1,2-Dichlorobenzene	2.931	0.756	7.53				
2-Methylphenol (o-cresol)	2.965	0.559	9.73				
Bis(2-chloro-1-methylethyl) ether	2.998	0.545	11.21				
1-Nitrosopyrrolidine	3.068	0.260	6.02				
p-Cresol	3.074	0.333	7.00				
N-Nitrosodi-n-propylamine	3.089	0.370	12.94				
Acetophenone	3.092	0.445	6.48				
4-Nitrosomorpholine	3.095	0.107	8.43				
o-Toluidine	3.116	0.487	8.39				
Hexachloroethane	3.180	0.112	8.62				
Nitrobenzene-d ₅	3.201	0.097	10.05				
Nitrobenzene	3.216	0.197	6.59				
Nitrosopiperidine	3.325	0.132	8.87				
Isophorone	3.395	0.433	7.86				
2-Nitrophenol	3.455	0.112	11.43				
2,4-Dimethylphenol	3.480	0.295	6.34				
Benzoic acid	3.519	0.117		0.9946	Linear	0.8	
Bis(2-chloroethoxy)methane	3.558	0.345	8.69				
2,4-Dichlorophenol	3.637	0.243	13.22				
1,2,4-Trichlorobenzene	3.710	0.356	10.34				
Naphthalene	3.773	0.978	8.27				
a,a-Dimethylphenethylamine	3.782	0.360		0.9976	Linear	0.2	
4-Chloroaniline	3.807	0.401	8.01				
2,6-Dichlorophenol	3.816	0.232	16.62				
Hexachlorobutadiene	3.873	0.177	19.36				

Name	Retention Time (min)	Average RF	Average RF %RSD	Curve Fit R ²	Curve Fit	Low Standard (µg/mL)	High Standard (µg/mL)
						Default is 0.1 to 100 µg/mL	
N-Nitrosobutylamine	4.079	0.172	9.34			0.2	
4-Chloro-3-methylphenol	4.185	0.204	10.56				
2-Methylnaphthalene	4.321	0.656	6.20				
Hexachlorocyclopentadiene	4.455	0.136		0.9928	Linear		
1,2,4,5-Tetrachlorobenzene	4.458	0.308	19.22				
2,4,6-Trichlorophenol	4.545	0.241	13.05				
2,4,5-Trichlorophenol	4.570	0.288	13.13				
2-Fluorobiphenyl	4.618	0.613	9.30				
1-Chloronaphthalene	4.715	1.018	9.32				
2-Chloronaphthalene	4.733	1.003	9.15				
2-Nitroaniline	4.791	0.226	14.72				
Dimethyl phthalate	4.948	1.005	10.34				
2,6-Dinitrotoluene	4.994	0.153	17.84			0.2	
Acenaphthylene	5.051	1.362	9.04				
m-Nitroaniline	5.124	0.178	10.30				
Acenaphthene	5.196	1.083	9.75				
2,4-Dinitrophenol	5.212	0.074	15.34			0.5	
4-Nitrophenol	5.260	0.143	18.74				
Pentachlorobenzene	5.305	0.428	14.62				
2,4-Dinitrotoluene	5.321	0.200	16.37				75
Dibenzofuran	5.339	1.486	9.57				
1-Naphthylamine	5.396	0.655	19.57				
2,3,4,6-Tetrachlorophenol	5.436	0.177		0.9912	Linear	0.5	
2-Naphthylamine	5.463	0.908	8.77				
Diethyl Phthalate	5.536	0.978	12.37			0.2	
Thionazin	5.599	0.142	16.65				
Fluorene	5.620	1.242	9.88				
5-Nitro-o-toluidine	5.623	0.209	19.75				
4-Chlorophenyl phenyl ether	5.623	0.530	15.50				
4-Nitroaniline	5.626	0.206		0.9943	Linear	0.2	
2-Methyl, 4,6-dinitrophenol	5.654	0.098	19.68			0.2	
Diphenylamine	5.717	0.943	9.95				
Azobenzene	5.754	0.397	5.84				
2,4,6-Tribromophenol	5.814	0.083	19.91				
Sulfotep	5.863	0.082		0.9976	Quadratic	0.2	
Diallate I	5.963	0.144	7.38				
Phorate	5.969	0.210	11.43				
Phenacetin	5.972	0.224	12.11				
4-Bromophenyl phenyl ether	6.026	0.197	8.23				
Diallate II	6.038	0.050	10.31				
Hexachlorobenzene	6.072	0.245	16.95				
Dimethoate	6.099	0.141	16.58				
4-Aminobiphenyl	6.235	0.611	10.94				

Name	Retention Time (min)	Average RF	Average RF %RSD	Curve Fit R ²	Curve Fit	Low Standard (µg/mL)	High Standard (µg/mL)
						Default is 0.1 to 100 µg/mL	
Pentachlorophenol	6.235	0.101		0.9911	Linear	0.5	
Pentachloronitrobenzene	6.247	0.054	19.27			0.5	
Propylamide	6.293	0.204	14.45				
Dinoseb	6.390	0.089	19.44				
Disulfoton	6.402	0.317		0.9966	Linear	0.5	
Phenanthrene	6.411	1.091	14.31				
Anthracene	6.453	1.009	11.90				
Methyl parathion	6.708	0.124	10.22				
Dibutyl phthalate	6.889	0.840	16.44				
Parathion	7.032	0.089	12.62				
4-Nitroquinoline-1-oxide	7.044	0.064	19.82				
Fluoranthene	7.395	1.188	8.54				
Benzidine	7.504	0.544	9.47				
Pyrene	7.580	1.207	8.59				
Aramite	7.710	0.044	18.03			0.2	
<i>p</i> -Terphenyl-d ₁₄	7.716	0.422	14.16				
Aramite II	7.770	0.044	12.41			0.2	
<i>p</i> -(Dimethylamino)azobenzene	7.834	0.195		0.9919	Linear	0.5	
Chlorobenzilate	7.876	0.294	10.53				
3,3'-Dimethylbenzidine	8.107	0.466	17.39				
Benzyl butyl phthalate	8.128	0.343		0.9926	Linear	0.5	
3,3'-Dichlorobenzidine	8.549	0.364		0.9939	Linear	0.5	
Benz[a]anthracene	8.570	1.443		0.9985	Linear	0.2	
Chrysene	8.600	1.047	11.58				
Bis(2-ethylhexyl) phthalate	8.612	0.502	17.43				
Di- <i>n</i> -octyl phthalate	9.118	0.832	16.61				
7,12-Dimethylbenz[a]anthracene	9.397	0.376		0.9947	Linear	0.8	
Benzo[b]fluoranthene	9.400	1.198	17.62				
Benzo[k]fluoranthene	9.421	1.170	16.60				
Benzo[a]pyrene	9.657	0.874	17.50				
3-Methylcholanthrene	9.954	0.328		0.9905	Linear	0.8	
Dibenz[a,j]acridine	10.523	0.594		0.9908	Linear	0.8	
Indeno(1,2,3-cd)pyrene	10.720	1.210	19.76				
Dibenz[a,h]anthracene	10.738	1.016	19.11				
Benzo[ghi]perylene	11.020	1.024	17.29				

As an example of full calibration range retention, Figure 5 compares the linear range for nitrobenzene in He carrier gas (Figure 5A), and in H₂ carrier gas with the HydroInert source (Figure 5B). The average RF %RSDs are remarkably similar between the results for He carrier gas and H₂ carrier gas with the HydroInert source, at 6.33% RSD for He carrier gas, and 6.59% RSD for H₂ carrier gas and the HydroInert source. The qualifiers and raw spectrum for nitrobenzene in this data set can be reviewed to verify consistent mass spectra and ion fragment ratios for the HydroInert source with H₂ carrier gas. Figure 6 shows (A) the nitrobenzene base peak EIC, (B) an overlay of the base peak and qualifier EICs, and (C) the raw

mass spectrum, at calibration level 8 (10 µg/mL). In Figure 6B, the qualifier EICs are scaled to match height, but the ratios between the qualifier ion and base peak are indicated in the upper left of the figure and the accuracy of the ratio to the quantitative method reference ratios. The reference ratio of 93 to 77 *m/z* for this quantitative method is 31; Figure 6B ratio of 93/77 was 35.1, which is within 20% of the expected ratio, and significant conversion of nitrobenzene to aniline was not observed. The retention of nitrobenzene and avoidance of hydrogenation is also shown in the raw spectrum of Figure 6C, where 93 *m/z* is not taller than 123 nor 77 *m/z*.

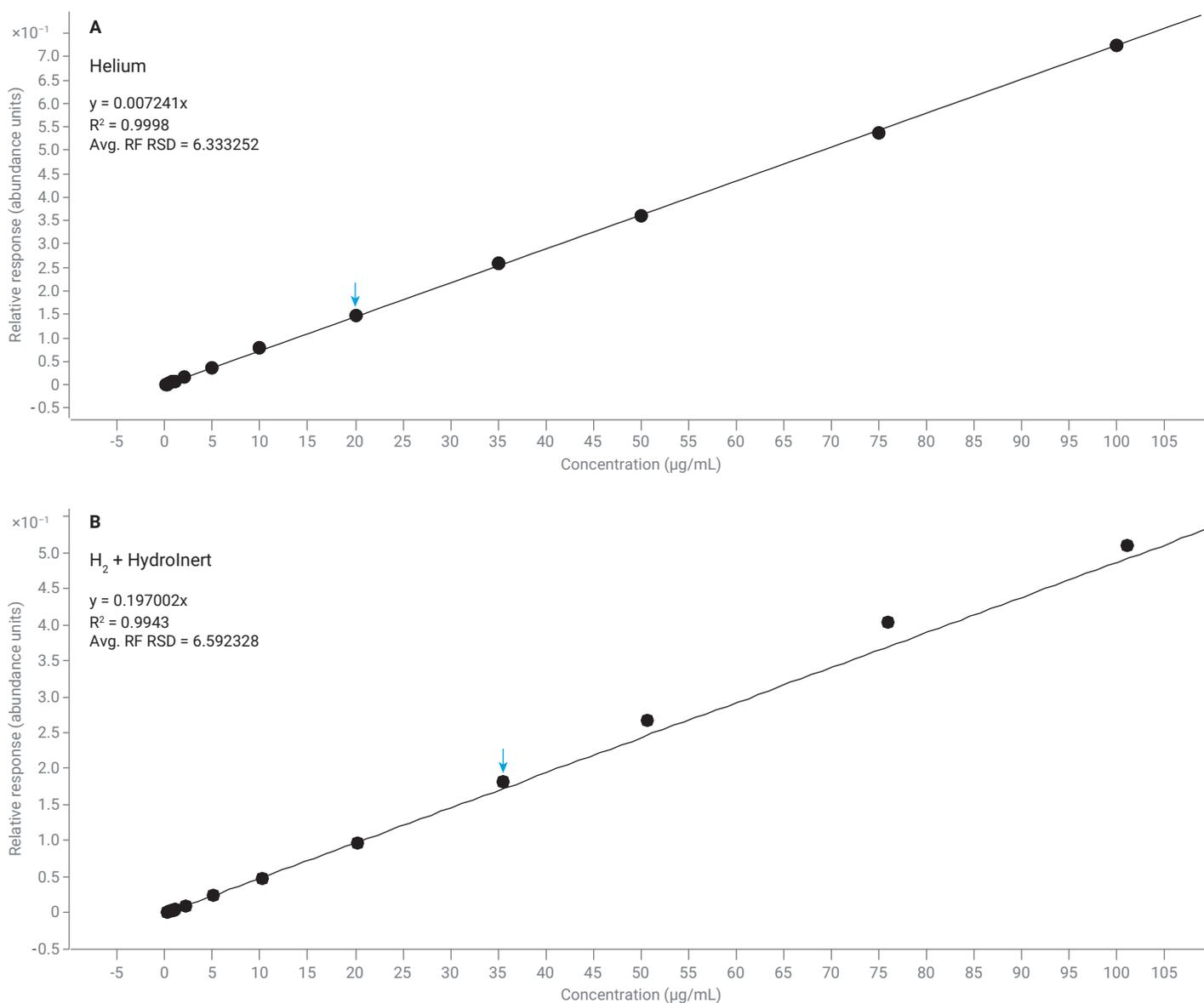


Figure 5. Nitrobenzene linear range (0.1 to 100 µg/mL) collected on a GC/MS system in (A) He and in (B) H₂ carrier gas with the Agilent HydroInert source.

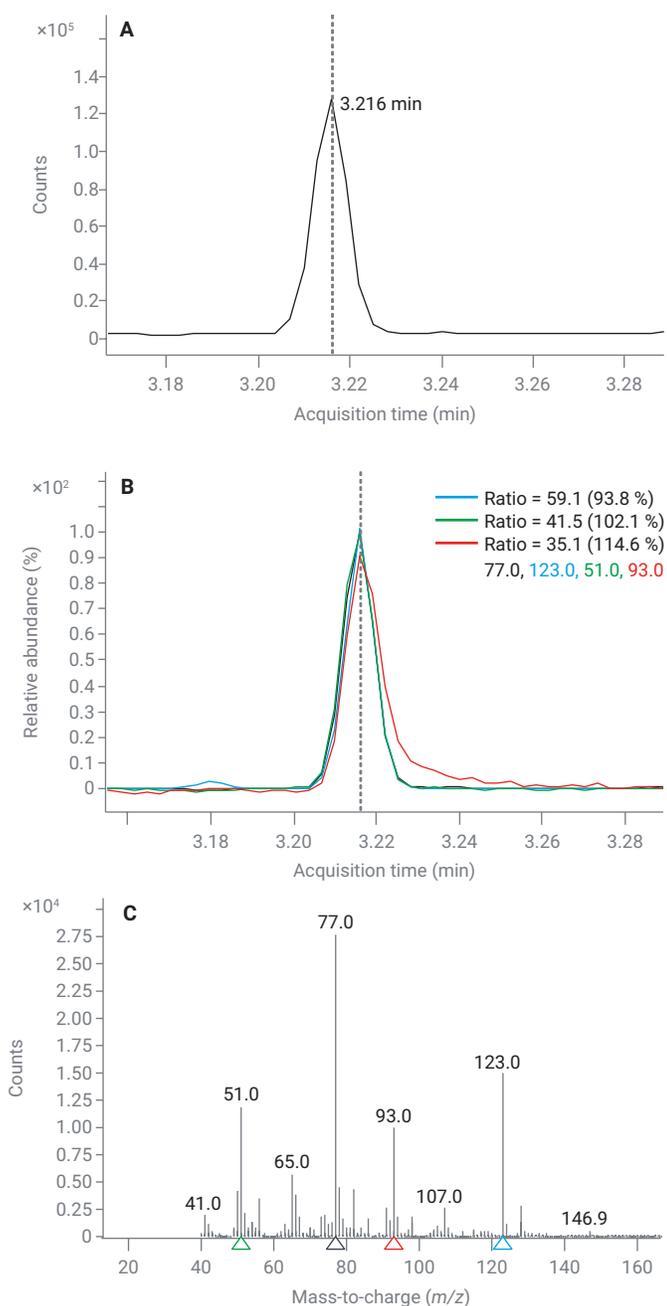


Figure 6. Nitrobenzene compound information for the 10 µg/mL standard; (A) extracted ion chromatogram (EIC 77 m/z) of the base peak; (B) overlay of base peak (77 m/z) and top three qualifier EICs (123, 51, 93 m/z); (C) raw mass spectrum for nitrobenzene peak at 3.216 minutes.

Repeatability in soil matrix

The large EPA method 8270 mixture of compounds was also diluted to a concentration of 15 µg/mL to act as a calibration verification standard, since 15 µg/mL was not a calibration point. To test the repeatability of the Hydrolnert source in GC/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 nine times. Table 7 contains the following data for each compound: average calculated concentration of the nine replicates of 15 µg/mL calibration verification in soil matrix and the %RSD for the nine replicate injections in soil matrix. Looking at the average calculated concentration of the 15 µg/mL sample in matrix, only two compounds are identified outside of the ±20% range for a calibration verification, which are both reported as lower concentrations: 5-nitro-*o*-toluidine and dibutyl phthalate. The two compounds are within 25% of the 15 µg/mL spike value, and the matrix may be causing a small amount of signal suppression. The %RSD for the replicate injections in soil matrix are all below 7% RSD, indicating that the method is robust and consistent.

Table 7. Average concentration (nine replicate injections) of the 15 µg/mL calibration verification standard in soil matrix and the %RSD of the nine replicate injections.

Name	Average Calculated Concentration in Matrix of 15 µg/mL Spike	%RSD of Nine Replicates
N-Nitrosodimethylamine	15.6	2.21%
Pyridine	17.6	3.16%
2-Picoline	14.9	1.35%
N-Nitroso-N-methylethylamine	15.8	1.26%
Methyl methanesulfonate	15.0	2.05%
2-Fluorophenol	15.9	1.82%
N-Nitroso-N-diethylamine	15.6	2.53%
Ethyl methanesulfonate	15.0	2.14%
Phenol-d ₆	15.6	1.91%
Phenol	15.1	1.00%
Aniline	15.7	1.62%
Bis(2-chloroethyl) ether	15.0	1.49%
2-Chlorophenol	15.1	1.54%
1,3-Dichlorobenzene	15.0	1.11%
1,4-Dichlorobenzene	14.4	1.31%
Benzyl alcohol	15.2	2.39%
1,2-Dichlorobenzene	15.3	1.86%
2-Methylphenol (<i>o</i> -cresol)	15.6	1.43%
Bis(2-chloro-1-methylethyl) ether	14.4	1.91%
1-Nitrosopyrrolidine	14.9	2.73%
<i>p</i> -Cresol	14.2	1.08%
N-Nitrosodi- <i>n</i> -propylamine	14.6	2.71%
Acetophenone	14.7	2.35%

Name	Average Calculated Concentration in Matrix of 15 µg/mL Spike	%RSD of Nine Replicates
4-Nitrosomorpholine	14.4	2.40%
<i>o</i> -Toluidine	14.4	1.26%
Hexachloroethane	15.0	4.80%
Nitrobenzene-d ₅	15.0	1.53%
Nitrobenzene	14.8	1.87%
Nitrosopiperidine	14.5	2.32%
Isophorone	14.7	2.52%
2-Nitrophenol	15.4	3.43%
2,4-Dimethylphenol	14.3	1.79%
Benzoic acid	14.3	6.81%
Bis(2-chloroethoxy)methane	14.8	1.73%
2,4-Dichlorophenol	14.9	1.64%
1,2,4-Trichlorobenzene	15.0	1.31%
Naphthalene	14.4	1.50%
<i>α,α</i> -Dimethylphenethylamine	14.0	2.25%
4-Chloroaniline	15.5	1.80%
2,6-Dichlorophenol	17.9	1.34%
Hexachlorobutadiene	13.5	3.66%
<i>N</i> -Nitrosobutylamine	14.2	2.45%
4-Chloro-3-methylphenol	15.1	2.29%
2-Methylnaphthalene	14.7	1.59%
Hexachlorocyclopentadiene	12.6	3.44%
1,2,4,5-Tetrachlorobenzene	14.9	2.77%
2,4,6-Trichlorophenol	15.3	1.92%
2,4,5-Trichlorophenol	15.3	1.91%
2-Fluorobiphenyl	15.5	1.47%
1-Chloronaphthalene	14.9	1.65%
2-Chloronaphthalene	15.3	1.64%
2-Nitroaniline	15.4	1.75%
Dimethyl phthalate	15.8	1.42%
2,6-Dinitrotoluene	13.1	3.81%
Acenaphthylene	15.0	1.03%
<i>m</i> -Nitroaniline	12.4	2.93%
Acenaphthene	14.5	1.52%
2,4-Dinitrophenol	12.3	5.97%
4-Nitrophenol	12.8	2.57%
Pentachlorobenzene	16.2	1.84%
2,4-Dinitrotoluene	15.6	2.45%
Dibenzofuran	14.9	1.23%
1-Naphthylamine	14.1	1.28%
2,3,4,6-Tetrachlorophenol	12.7	3.86%
2-Naphthylamine	14.7	1.26%
Diethyl phthalate	14.4	2.21%
Thionazin	14.0	2.99%
Fluorene	14.2	1.72%
4-Chlorophenyl phenyl ether	14.4	2.41%
5-Nitro- <i>o</i> -toluidine	11.4	4.16%
4-Nitroaniline	14.9	3.37%

Name	Average Calculated Concentration in Matrix of 15 µg/mL Spike	%RSD of Nine Replicates
2-Methyl, 4,6-dinitrophenol	13.6	2.93%
Diphenylamine	15.2	0.66%
Azobenzene	14.8	2.76%
2,4,6-Tribromophenol	15.5	3.74%
Sulfotep	13.1	4.28%
Diallate I	15.6	3.38%
Phorate	14.9	2.14%
Phenacetin	16.1	2.66%
4-Bromophenyl phenyl ether	14.8	2.08%
Diallate II	14.9	3.70%
Hexachlorobenzene	16.9	2.73%
Dimethoate	12.7	2.42%
Pentachlorophenol	13.4	4.84%
4-Aminobiphenyl	16.0	2.40%
Pentachloronitrobenzene	16.7	6.40%
Propyzamide	15.2	2.86%
Dinoseb	13.0	3.24%
Disulfoton	14.2	4.39%
Phenanthrene	14.5	0.88%
Anthracene	15.0	2.01%
Methyl parathion	15.5	3.70%
Dibutyl phthalate	11.5	3.70%
Parathion	15.7	2.21%
4-Nitroquinoline-1-oxide	16.9	2.04%
Fluoranthene	15.0	0.95%
Benzidine	14.0	2.76%
Aramite	13.9	3.71%
Aramite II	13.3	3.59%
Pyrene	14.8	1.62%
<i>p</i> -Terphenyl-d ₁₄	15.3	1.98%
<i>p</i> -(Dimethylamino)azobenzene	14.0	2.05%
Chlorobenzilate	14.9	1.92%
3,3'-Dimethylbenzidine	14.6	2.11%
Benzyl butyl phthalate	13.8	2.51%
3,3'-Dichlorobenzidine	15.8	1.90%
Benz[<i>a</i>]anthracene	13.7	0.98%
Chrysene	14.5	1.31%
Bis(2-ethylhexyl) phthalate	15.2	1.89%
Di- <i>n</i> -octyl phthalate	14.3	1.30%
7,12-Dimethylbenz[<i>a</i>]anthracene	12.2	1.40%
Benzo[<i>b</i>]fluoranthene	14.7	1.50%
Benzo[<i>k</i>]fluoranthene	15.4	2.94%
Benzo[<i>a</i>]pyrene	15.4	2.07%
3-Methylcholanthrene	14.6	2.77%
Dibenz[<i>a,j</i>]acridine	13.0	1.58%
Indeno(1,2,3- <i>cd</i>)pyrene	15.8	1.44%
Dibenz[<i>a,h</i>]anthracene	15.5	2.18%
Benzo[<i>ghi</i>]perylene	15.5	1.56%

Conclusion

A method for testing SVOCs using H₂ carrier gas and the Agilent HydroInert source, which prevents hydrogenation and dechlorination of target analytes, has been developed for the Agilent 5977B Inert Plus GC/MSD. Method criteria for EPA method 8270D/E are met for the GC/MS tuning mixture, DFTPP tuning criteria, and initial calibration over the normal working range of 0.1 to 100 µg/mL in a single 12-minute run, with 15 compounds of the 119 tested compounds requiring curve fits. 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.

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