Agilent
Trusted Answers

Enable Hydrogen Carrier Gas Selections without Compromising GC/MS Performance

Application Compendium

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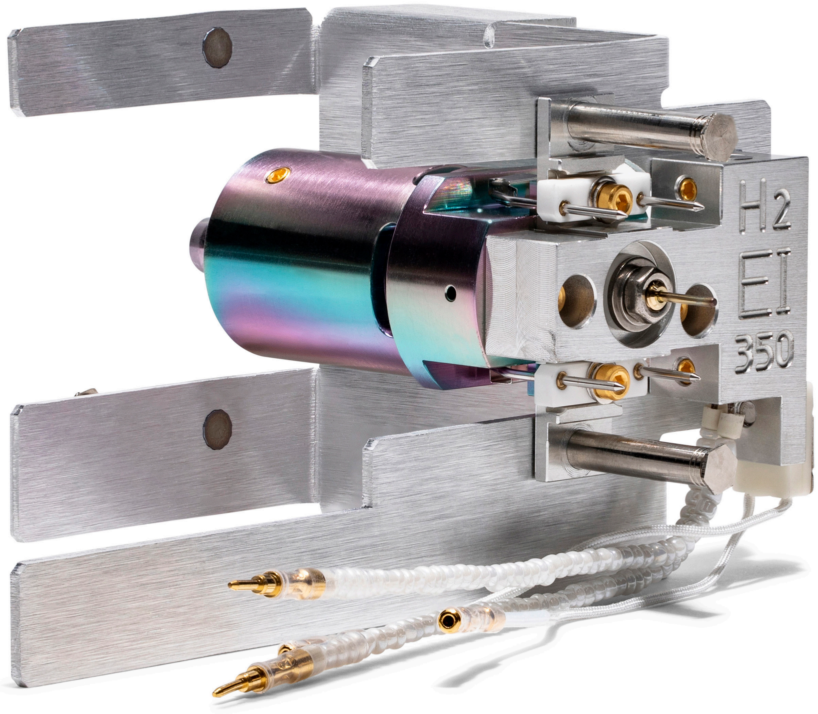
Introduction

Recent helium shortages have become acute in many regions, resulting in price increases, and even stopped shipments. These shortages jeopardize the operations of labs that depend on gas chromatography. Hydrogen (H_2) being a low-cost and easy to procure gas is a good alternative to helium, however, owing to its non-inert nature, it causes unwanted reactions in the MS source. The Agilent HydroInert source addresses this problem and is ideal for labs that are considering hydrogen but are worried about analytical limitations. HydroInert allows you to:

- Prevent work stoppages caused by insufficient helium supplies
- Reduce sensitivity loss and spectral anomalies
- Achieve faster, shorter separations
- Minimize downtime caused by system maintenance and ion source cleaning



Agilent HydroInert source

Technical Overview

Agilent Inert Plus GC/MS System with HydroInert Source

Applying H_2 carrier gas to real-world GC/MS analyses

Introduction

With increased price and pressure on the helium (He) market, laboratories are looking for a more sustainable alternative to helium and exploring the option of hydrogen (H_2) carrier gas. The benefits of hydrogen in gas chromatography (GC) are widely accepted, as it can be generated in the lab in a cost-effective manner and produces fast chromatography and higher sample throughput. Since hydrogen is a reactive gas, hydrogenation and dechlorination reactions can and do occur in the mass spectrometer electron ionization (EI) source. These reactions can make applying hydrogen carrier gas to many applications difficult. A newly designed extractor source for the Agilent 5977B Inert Plus GC/MSD and Agilent 7000D/E Inert Plus triple quadrupole GC/MS systems address these hydrogen-related issues and help improve performance with hydrogen carrier gas in GC/MS and GC/MS/MS. The Agilent HydroInert source with H_2 carrier gas retains mass spectral fidelity and can allow users to continue to use existing helium-based mass spectral libraries.

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Transitioning from helium to hydrogen

Considerations for applying H_2 to GC/MS analyses have been discussed in previous literature.[1] These considerations, especially the focus on GC parameters for optimal separation, remain valid with the HydroInert source for Inert Plus mass spectrometer systems. While helium is the best carrier gas for GC/MS, the HydroInert source was developed to work with hydrogen carrier gas, which is the best alternative when helium is not available.

Some of the considerations are summarized in a shortened list below:

- It is highly recommended that stainless steel tubing be used with H_2. If only copper tubing is available, install fresh copper lines. A stainless steel installation kit of fittings and tubing is available under part number 19199S.
- Always use gas filters, especially with H_2 generators. The recommendation is to install an Agilent big universal trap (for moisture, O_2, and hydrocarbons) for H_2 (part number RMSH-2-SS) and an Agilent Gas Clean purifier for carrier gas (part number CP17976 for the kit including a base, or part number CP17973 for a replacement carrier gas filter if you already have the base).
- Decrease inlet temperature when working with sensitive compounds, or use cold splitless injection with multimode inlet, where possible.
- Hydrogen viscosity is lower than helium, causing lower inlet pressures. It is advisable to at least:
  - Change column dimensions, or
  - Increase the carrier gas flow rate
- Optimal carrier gas flows depend on the pump, as pumping capacity for hydrogen is lower than helium.
  - Optimal range: 0.5 to 1.0 mL/min
  - Maximum recommended flow rate for turbo pump: 2.0 mL/min
- Use constant flow methods.
- For GC/MS/MS systems running hydrogen, no quench gas (helium) is used. Please remove the helium plumbing from the back of the electronics pressure control module (EPC) and set the quench gas to 0.00 mL/min in any GC/MS/MS method.

Changes will be required in most cases, and it is necessary to allot time for necessary updates to standard operating procedures (SOPs) and method validation.

HydroInert source

The HydroInert source, shown in Figure 1, is a novel source based on the Agilent extractor source design. The HydroInert source is an easy conversion from the existing EI extractor or EI Inert Plus sources in both the single quadrupole (Agilent 5977B or 5977C GC/MSD) and the triple quadrupole (Agilent 7000D or 7000E triple quadrupole GC/MS) systems. Do not mix the HydroInert source parts with the extractor source parts; this can cause unexpected and unwanted results, especially when using hydrogen carrier gas.

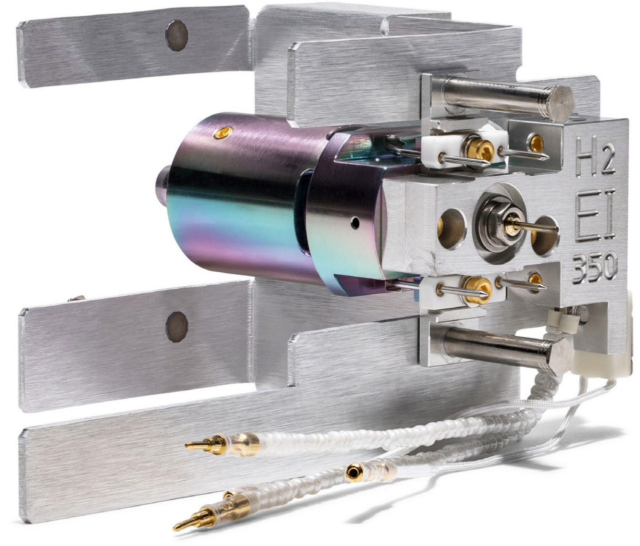


Figure 1. Agilent HydroInert source.

Usually, there would be a note about hydrogenation or dechlorination of certain compound classes when using H_2 with GC/MS systems, along with a discussion about the need to build internal compound libraries or understanding that library match scores with the NIST or other helium-based libraries may not match well with hydrogen mass spectra. However, the HydroInert source is more inert to H_2, and the mass spectra retain their normal characteristics observed in He mass spectra.

Here is a primary example of the benefits of the HydroInert source with nitrobenzene. In an experiment with an extractor source with a 3 mm extraction lens, hydrogen was used as the carrier gas for testing semivolatile organic compound (SVOC) analysis. Nitrobenzene was one of the compounds in the mixture (part number SVM-122-1). Nitro compounds are known to be susceptible to hydrogenation when in the presence of heat, hydrogen, and metal surfaces; all these factors are present in the extractor source. Hydrogenation of nitrobenzene (molecular weight (MW) 123 *m/z*) will form aniline (MW 93 *m/z*). When reviewing the mass spectrum under the total ion chromatogram (TIC) peak for the extractor source and H_2 carrier gas, the mass spectrum in Figure 2A 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.

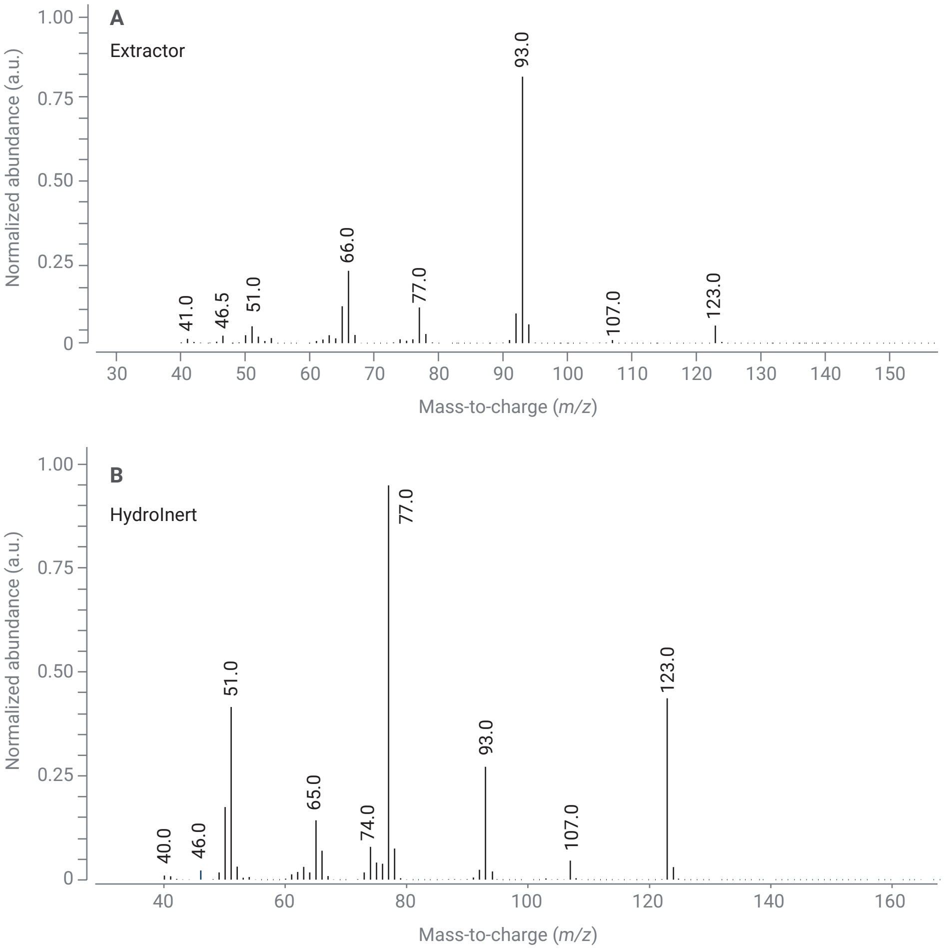


Figure 2. Mass spectra for peak eluting at nitrobenzene retention time with hydrogen carrier gas in (A) extractor source with 3 mm extraction lens showing hydrogenation to aniline with the abundant 93 *m/z* ion and (B) Agilent HydroInert source, showing an improved mass spectrum that correlates to nitrobenzene.

Comparatively, the same mixture containing nitrobenzene was tested on a HydroInert source (with a 9 mm extraction lens), where we observe the expected distribution of 123 *m/z* and 93 *m/z* in the mass spectrum (Figure 2B), indicating 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 Figures 3A (the extractor source conversion) and 3B (for HydroInert source retention of nitrobenzene), where we observe an improved 123/93 ratio using the HydroInert source, while the extractor source EIC overlay shows significant conversion to 93 *m/z* and significant tailing.

Mass spectral fidelity examples

Nitrobenzene is one example of mass spectral fidelity occurring with H_2 carrier gas and the HydroInert source. Other nitro compounds can also have hydrogenation issues in the presence of H_2, whether the compound is a pesticide, SVOC, or other compound class. Chlorinated compounds can also dechlorinate in the presence of H_2 carrier gas and metal or other active sites; dichlorodiphenyltrichloroethane (DDT) is a common compound that has breakdown issues in GC inlets due to heat and active sites, like metal, but can also be affected by dechlorination in a source in the presence of hydrogen. DDT was analyzed by He carrier gas and then with H_2 carrier gas using the extractor source and a pair of columns, to match retention times generated from the He carrier gas method. Commonly, two Agilent J&W HP-5ms Ultra Inert GC columns, 15 m × 0.25 mm, 0.25 µm, are used for pesticide analysis. For hydrogen, the columns were changed to two Agilent J&W HP-5ms Ultra Inert GC columns, 20 m × 0.18 mm, 0.18 µm, to match the retention times and avoid having to reset many retention times for a method containing hundreds of pesticides. Based on the helium results, DDT eluted at 13.04 minutes, while dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) eluted earlier at 12.44 and 12.88 minutes, respectively. Looking at the results for H_2 carrier gas and the extractor source at 13.04 minutes, DDD was identified instead of DDT, as indicated in Table 1. With the HydroInert source and H_2 carrier gas, DDT was accurately identified at 13.04 minutes, with a library match score of 85 (compared to NIST17.L library). This misidentification at 13.04 minutes for the extractor source (and hydrogen carrier gas) occurred across multiple

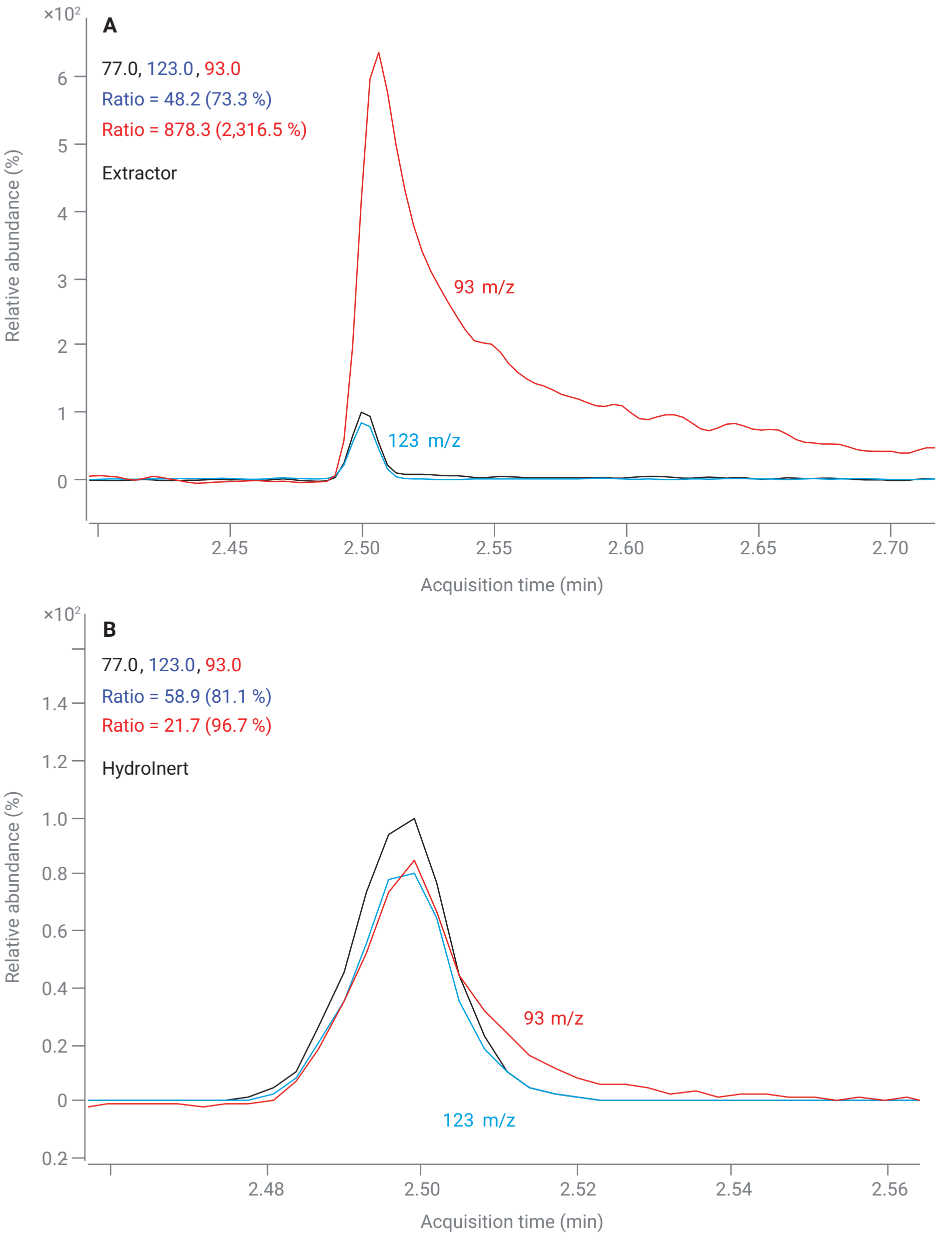


Figure 3. EICs of nitrobenzene with hydrogen carrier gas in (A) extractor source with 3 mm extraction lens, showing hydrogenation to aniline with the abundant 93 *m/z* ion and (B) Agilent HydroInert source, showing an improved 123 versus 93 *m/z* ratio.

Table 1. Comparison of extractor and Agilent HydroInert sources when using H_2 carrier gas for identification of DDT and DDT breakdown products.

Source with H_2 Carrier Gas	Retention Time (min)	Identified Compound	Library Match Score
Extractor	13.04	DDD	79
HydroInert	13.04	DDT	85

runs, indicating that DDT was being dechlorinated in the source to DDD. In both HydroInert and extractor source systems, DDE and DDD were also identified at their respective retention times (12.44 and 12.88 minutes), showing that there was <10% DDT breakdown occurring in the inlet as well. The inlet breakdown was not the focus of this testing set; optimizing the injection parameters and liner can decrease the DDT breakdown, as could lowering inlet temperatures or using cold splitless injection with a multimode inlet.

Another chlorinated compound example can be observed with heptachlor. Using the same experimental design as nitrobenzene, an extractor source with a 3 mm extraction lens was installed in a GC/MS single quadrupole instrument with H_2 carrier gas, which is the recommended extraction lens for pesticide analysis with He. A mixture of pesticides (part number PSM-105-A), including heptachlor, was diluted to 10 ng/µL and a set of deuterated polycyclic aromatic hydrocarbons (PAHs) was added as internal standards. The deconvoluted mass spectrum of heptachlor is shown in Figure 4A with a head-to-tail comparison with the NIST17.L library mass spectrum of heptachlor. The most abundant ions should be 272, 274, 270, 100, and 65 *m/z*, but Figure 4A and Figure 5A display a significant increase in ion abundance for the ions around 235 and 237 *m/z*, causing them to be in the top five most abundance ions, while the 272 and 274 *m/z* are suppressed. Only 272 *m/z* is found in the top five most abundant EICs, and 165 *m/z* has significant contribution as an EIC, which should have little-to-no intensity. Also, two of the five EICs, 66 and 272 *m/z*, have different peak apices than the other three. This swap in higher-abundance regions from the 272 to 235 *m/z* region, change in the highest abundance ions, and mismatched peak apexes indicates dechlorination

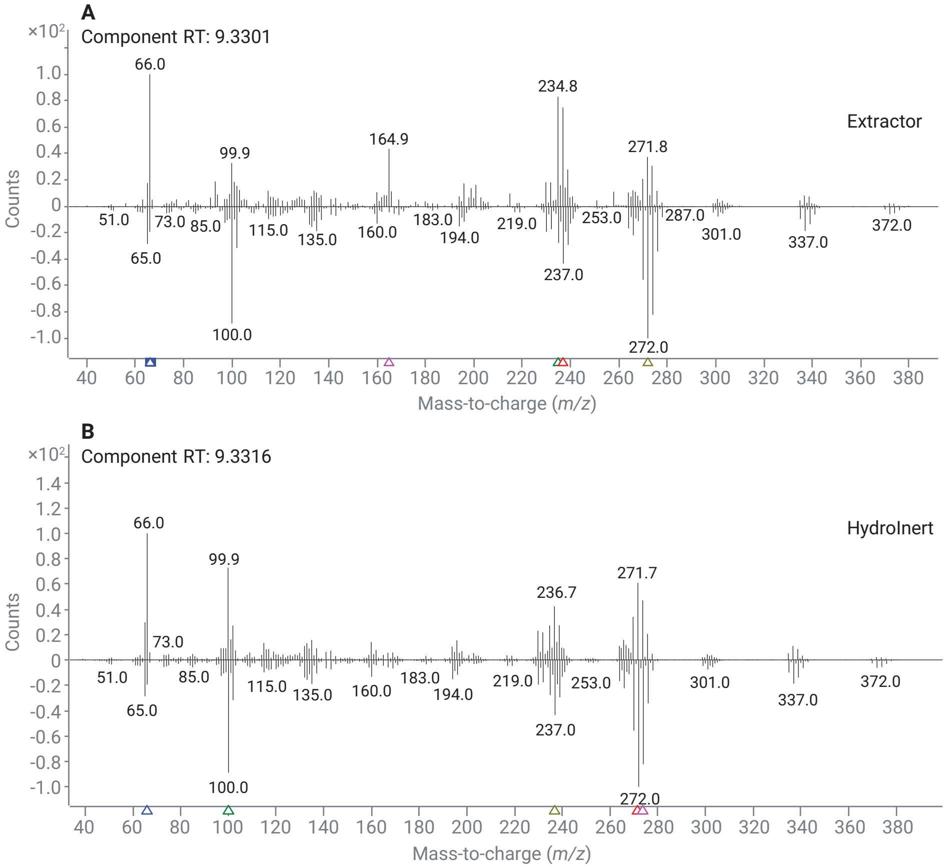


Figure 4. Head-to-tail comparison of deconvoluted mass spectrum (top) to library mass spectrum, NIST17.L (bottom) for heptachlor with H_2 carrier gas and (A) extractor source with 3 mm extraction lens and (B) Agilent HydroInert source with 9 mm extraction lens.

reactions occurred in the source. Comparatively, results for H_2 carrier gas and the HydroInert source with a 9 mm extraction lens are shown in the extracted mass spectrum in Figure 4B, and the top five abundant EICs in Figure 5B. In Figure 4B, 272 *m/z* region is higher than the 237 *m/z* region, and there is a significant abundance to 100 *m/z*, like the reference library spectrum on the bottom of the head-to-tail comparison, indicating retention of chlorine atoms. Additionally, the top five EICs for the HydroInert results have aligned peak apices and include three of the expected ions: 272, 274, and 100 *m/z*; ions 237 and 270 *m/z* are close in abundance with 237 *m/z* slightly taller and edging out 270 *m/z* to reach the top five EICs.

Library match scores examples

Since the HydroInert source prevents compound breakdown, hydrogenation, and dechlorination in the presence of hydrogen, libraries of mass spectra collected with helium can be used with the HydroInert source and H_2 carrier gas. We completed experiments to evaluate the use of a large general library, such as the NIST library, when using He or H_2 carrier gas with extractor and HydroInert sources, with their respective 9 mm extraction lenses, as follows: an extractor source with He carrier gas, an extractor source with H_2 carrier gas, and a HydroInert source with H_2 carrier gas. A mixture of SVOCs, pesticides, and fragrance compounds was generated with a set of six deuterated PAHs at 10 ng/µL to run across all three source experiments on an Agilent 8890 GC with a 5977 Inert Plus single quad mass spectrometer in scan mode. The data were loaded into Agilent MassHunter Unknowns Analysis software and a deconvolution method was applied using the NIST17.L library to evaluate library match scores (LMS).

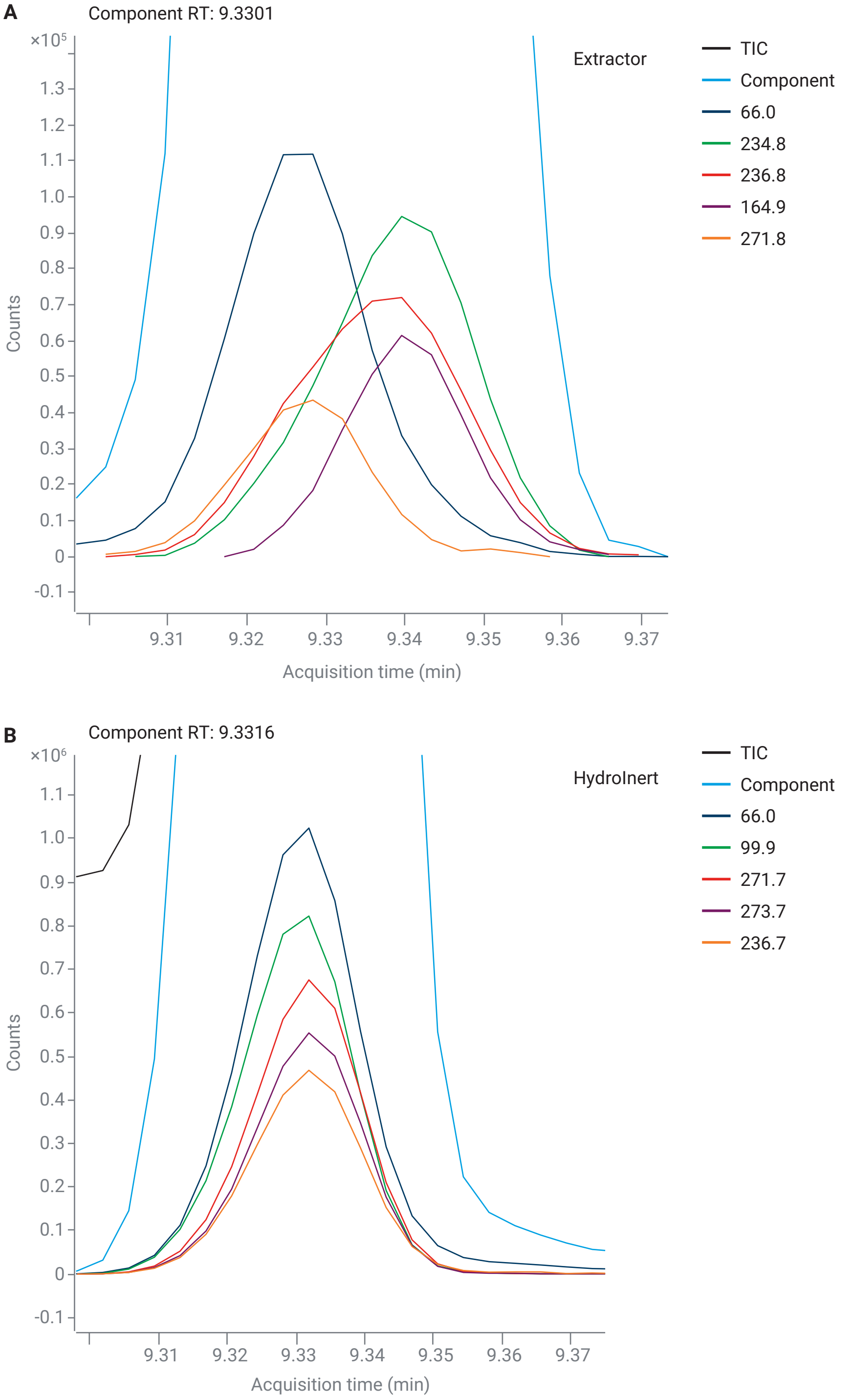


Figure 5. EICs of the top five abundant ions for heptachlor with H_2 carrier gas and (A) extractor source with 3 mm extraction lens and (B) Agilent HydroInert source with 9 mm extraction lens.

The helium carrier gas with extractor source LMS values in Table 2 are used as the baseline values to compare to H_2 carrier gas with an extractor source (center column) or the HydroInert source (right column). All the LMS values for the HydroInert source are within five percentage points of the helium LMS values, where some of the LMS values for the HydroInert source with H_2 are better matches to the NIST library, for example 4-nitrophenol and benzidine. Fifteen of the HydroInert collected LMS values are within two percentage points of the He collected data and five LMS values for HydroInert source are three or more percentage points higher than the He collected LMS values, such as musk ambrette and benzidine. This retention of high LMS values with H_2 carrier gas and HydroInert source indicates retention of functional groups and mass spectral fidelity in the source. However, the H_2 carrier gas and extractor source has 10 compounds with LMS values lower by five percentage points or more compared to the H_2 HydroInert LMS values. Some LMS values for the extractor source are as low as 70, such as benzidine and benzo(b)fluoranthene, indicating that hydrogenation or other conversions are occurring in the extractor source with H_2 carrier gas. As expected, the chlorinated compounds and nitro compounds were affected by the H_2 carrier gas and extractor source with lower library match scores, including nitrobenzene (80.9 LMS), 4-nitrophenol (83.1 LMS), pentachlorophenol (85.4 LMS), fenitrothion (88.3 LMS), and musk ketone (89.8 LMS). These scores are still relatively high, but as concentrations drop and identifications become more difficult, the conversion of compounds in the source becomes more problematic. In summary, HydroInert source with H_2 carrier gas retains mass spectral fidelity and can allow users to continue to use existing He-based mass spectral libraries.

Table 2. Comparison of LMS for a mixture of SVOCs, pesticides, and fragrance compounds using an extractor source with He carrier gas, an extractor source with H_2 carrier gas, and an Agilent HydroInert source with H_2 carrier gas.

Analyte	Extractor He LMS	Extractor H_2 LMS	HydroInert H_2 LMS
Aniline	98.6	92.3	97.7
1,4-dichlorobenzene-d_4	96.7	94.7	97.5
Nitrobenzene	95.7	80.9	94.3
Benzoic acid	93.3	87.7	97.2
Naphthalene-d_8	96.9	93.9	97.6
Acenaphthene-d_{10}	98.3	97.3	97.8
2,4-dinitrophenol	95.6	90.6	94.8
4-nitrophenol	89.5	83.1	94.8
4,6-dinitro-2-methylphenol	94.3	93.6	95.7
Pentachlorophenol	90.7	85.4	89.1
4-aminobiphenyl	96.9	95.8	97.9
Phenanthrene-d_{10}	97.7	93.3	97.2
Musk ambrette	86.6	86.3	89.5
Fenitrothion	95.6	88.3	97.0
Musk ketone	95.8	89.8	98.2
Benzidine	92.6	70.1	97.5
3,3'-dichlorobenzidine	97.3	89.8	95.3
Chrysene-d_{12}	96.0	84.8	93.5
Benzo[b]fluoranthene	97.8	70.1	98.4
Benzo[k]fluoranthene	97.8	96.8	98.4
Perylene-d_{12}	94.4	79.4	93.1

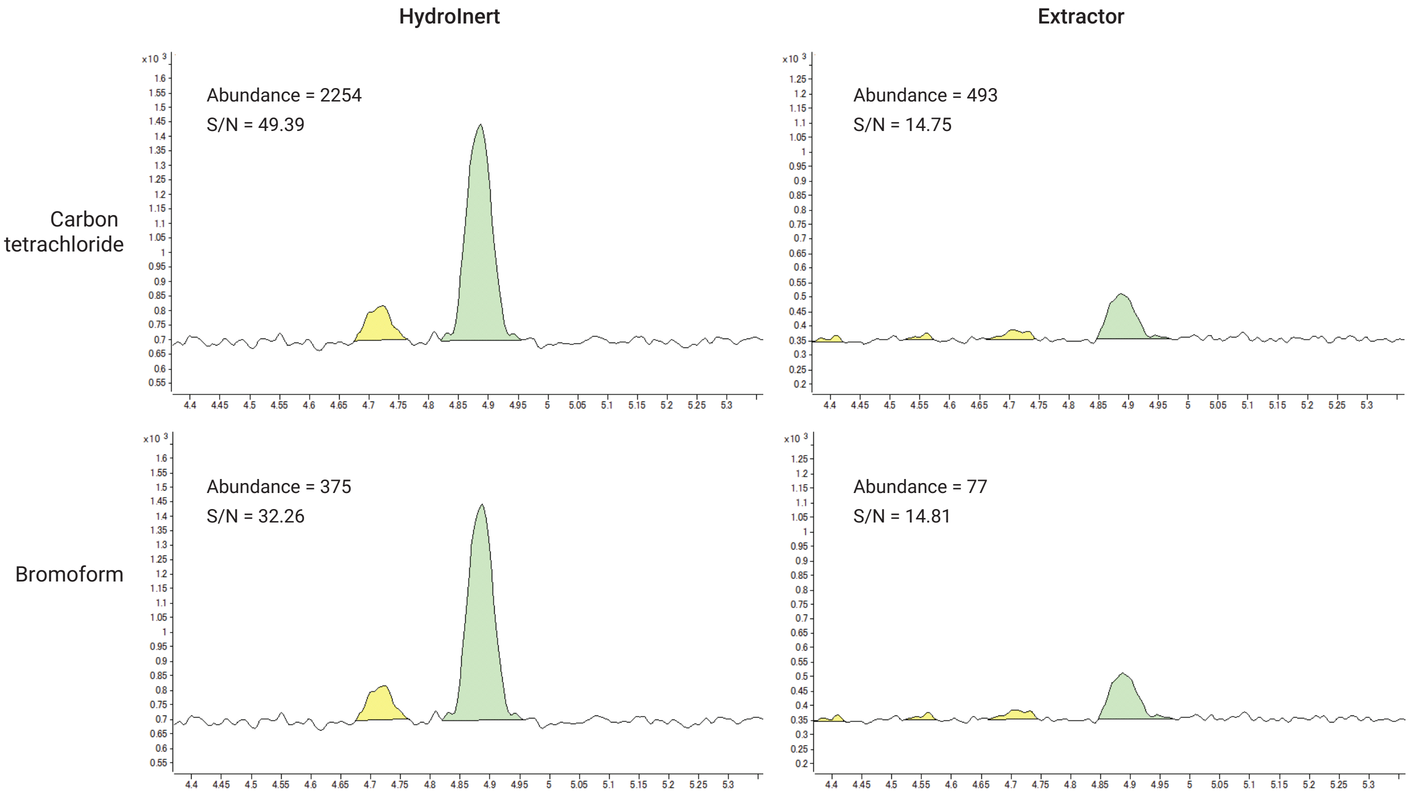
Reduced source cleaning

One of the advantages observed with hydrogen carrier gas is a reduced EI source cleaning. This has been observed when using Agilent Jet Clean self-cleaning ion source, which introduces a low flow of hydrogen into the source during or after analysis.[2] The reduction of source cleaning is also observed with the HydroInert source. A set of experiments was completed to investigate source lifetime using a complex soil matrix and Environmental Protection Agency (EPA) method 8270 target analytes and quality control criteria to evaluate when the GC or MS required maintenance. One set of experiments used He carrier gas with an extractor source and 9 mm extraction lens; the other experiment set used H_2 carrier gas with the HydroInert source and 9 mm (HydroInert) extraction lens. The He GC/MS system required source cleaning after an average of 365 matrix injections (581 total injections). For the HydroInert source, 5,200 matrix injections were completed before the source failed acceptance criteria. The HydroInert extraction lens and repeller were replaced and retuned, and the system was able to recover to acceptable performance. At this time, the HydroInert extraction lens and repeller are recommended to be replaced if found to be dirty, and method criteria cannot be recovered with GC maintenance. The extraction lens insulator (part number G3870-20445) may also be replaced at the same time, as the ceramic insulators can become dirty over time.

Sensitivity

Depending on the application, sensitivity is affected by the introduction of H_2 carrier gas, especially when using existing MS sources like the extractor source. Users tend to see decreased signal-to-noise ratios (S/N) and potentially reduced linear ranges for calibration or higher limits of detection (LOD) due to higher background caused by hydrogen interactions. With the HydroInert source for select applications, we have observed increased S/N values or abundance for compounds compared to the extractor source. For example, volatile organic compounds (VOCs) were tested in water samples using an Agilent 7697A headspace sampler, 8890 GC, and 5977 Inert Plus GC/MSD to compare sensitivity and S/N for the extractor source and HydroInert source with H_2 carrier gas. For two example compounds, bromoform and carbon tetrachloride, increases in abundance and S/N are observed in Figure 6. In the same analysis, 1,4-dioxane exhibited increased abundance with the HydroInert source, but similar S/N to the extractor source results (Figure 7). Not every compound, matrix, nor analysis will have the same or improved results, and should be tested in a limited capacity before transferring multiple instruments to hydrogen.

To probe the sensitivity of the HydroInert source with H_2 carrier gas, octafluoronaphthalene (OFN) at 10 fg/µL (part number 5190-0585) was procured for GC/MS/MS sensitivity testing. For the tandem quadrupole GC/MS/MS system, 4 fg is the maximum allowable instrument detection limit (IDL), and values at 4.0 fg or lower are considered a pass. Four data sets of 12 OFN injections were completed to evaluate the IDL of the HydroInert source with H_2 carrier gas installed in an 8890 GC and 7000E triple quadrupole GC/MS system. The four IDL values were 2.1, 4.0, 2.0, and 3.5 fg for an average of 2.9 fg IDL, all of which pass the criteria.



S/N is calculated by peak-to-peak

Figure 6. Comparison of the Agilent HydroInert source and extractor source EICs for carbon tetrachloride and bromoform when using hydrogen carrier gas with a focus on abundance and S/N.

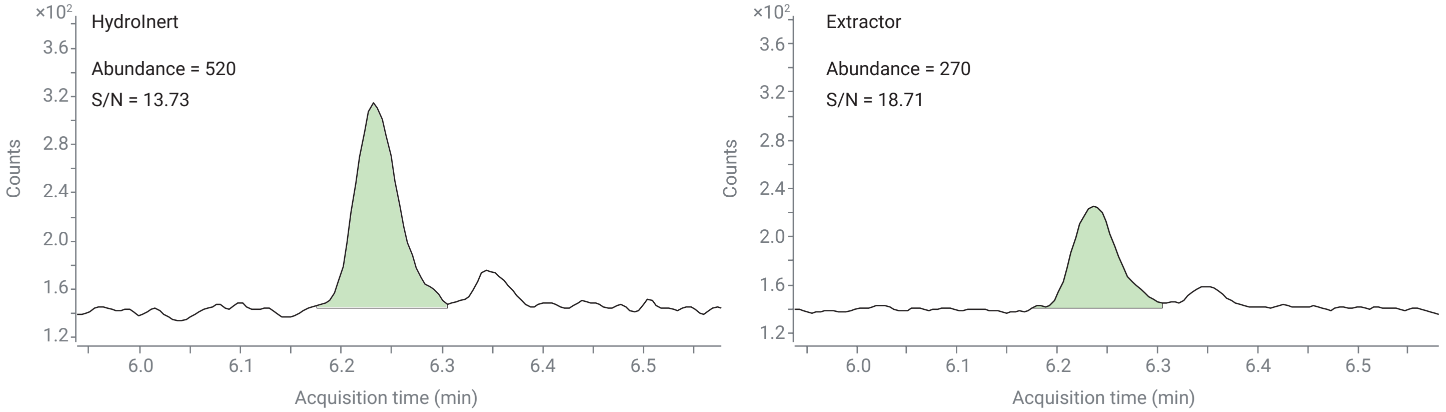


Figure 7. Comparison of the Agilent HydroInert source and extractor source EICs for 1,4-dioxane when using hydrogen carrier gas with a focus on abundance and S/N.

Tested applications

A set of applications was selected to evaluate the HydroInert source with H_2 GC/MS and GC/MS/MS analyses. The following sections highlight the results of using H_2 carrier gas and the HydroInert source for SVOC analysis, pesticide analysis, PAHs, and others. Based on the testing, Table 3 was generated to summarize the performance of a HydroInert Inert Plus system compared to the normal Inert Plus system when using H_2 carrier gas. Results were identified as "unacceptable" if the mass spectra had changes in ion fragment distribution, and misidentification of compounds due to breakdown, hydrogenation, or dechlorination. Some applications have comparable results with respect to mass spectral fidelity between the "normal" GC/MS system and HydroInert system using the respective 9 mm extraction lenses, such as hydrocarbon and PAH analyses, and were identified as "neutral" applications. Applications were identified to have "differentiating" results when the HydroInert source (in the presence of H_2 carrier gas) retained mass spectral fidelity and compounds were identified correctly with a helium library as reference.

Table 3. Tested compound classes, including example compounds, with performance abilities for hydrogen carrier gas with a typical Inert Plus source and the Agilent HydroInert source.

Compound Class	Example Compound(s)	H_2 Carrier Gas + Normal GC/MS Source	H_2 Carrier Gas + HydroInert Source
Nitro Compounds	Nitrobenzene, fenitrothion, ethalfluralin	Unacceptable	Differentiating
Heavily Chlorinated Compounds	DDT, Endrin, heptachlor, BHC compounds, pentachlorophenol	Unacceptable	Differentiating
PAHs	Benzo(b)fluoranthene, benzo[g,h,i]perylene, fluoranthene	Neutral	Neutral
Alkanes >C_{24}	Tetracosane (C_{24}), octatriacontane (C_{38})	Neutral	Neutral
Pesticides	Deltamethrin, fipronil, permethrin, captan	Unacceptable	Differentiating
Fragrance/Flavor Compounds	Musk ketone, musk ambrette, linalool	Unacceptable	Differentiating
VOCs	1,4-dioxane, trichloromethane, bromodichloromethane	Neutral	Differentiating

– "Unacceptable" was declared when mass spectral infidelity or compound misidentification was observed.
– "Neutral" was determined when results were similar across the normal GC/MS system and HydroInert source in the presence of hydrogen carrier gas.
– "Differentiating" was stated when the HydroInert source retained mass spectral fidelity and compounds were identified correctly with a helium library as reference.

Hydrocarbons

A hydrocarbon "ladder" from *n*-decane (C_{10}) to *n*-octatriacontane (C_{38}) can be used to evaluate cold spots and activity in a GC/MS system, where the high molecular weight compounds will have poor peak shape and significant tailing (>2.0), especially when using H_2 carrier gas. Specifically, for comparison of existing extractor source to the HydroInert source, the tailing factor of each straight-chain hydrocarbon peak was reviewed to verify that the HydroInert source did not exhibit a worse peak shape. The HydroInert TIC is displayed in Figure 8A and the existing extractor source TIC for the hydrocarbons is shown in Figure 8B. TIC comparison shows significant peak tailing for the extractor source with H_2 carrier gas starting at C_{22} (tailing factor of 1.27), increasing to a tailing factor of 2.1 for C_{26}, and continuing to increase up to extreme tailing with C_{38} (tailing factor of 10.2). Meanwhile, the TIC for HydroInert source data shows improved peak shape with tailing factors ranging between 0.6 to 0.9, where ideal tailing factor is 1.0. The improved peak shape with HydroInert source and H_2 carrier gas indicates thermal stability and lessened activity in the mass spectrometer, compared to the existing extractor source with H_2 carrier gas.

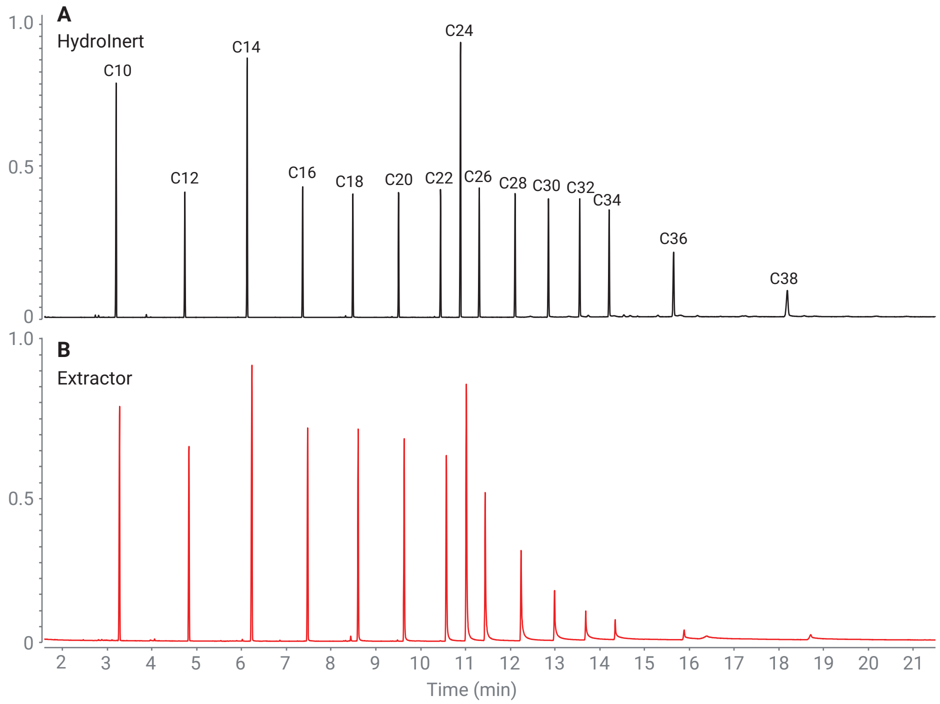


Figure 8. TICs of straight-chain hydrocarbons from *n*-decane (C_{10}) to *n*-octatriacontane (C_{38}) to visually represent the observed tailing (or lack thereof) when using hydrogen carrier gas with the (A) Agilent HydroInert source and (B) existing extractor source.

Semivolatile compounds analysis: EPA 8270 and PAHs

The United States 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.[3,4] Method 8270 contains SVOCs across several analyte class types from acids, bases, neutral compounds, and PAHs; to understand the application range and limit of the HydroInert source EPA 8270 analytes were tested, due to the wide range of compound classes and application uses in laboratories. The screening mixture in Table 2 is comprised of many semivolatile compounds that are found in the EPA method 8270 list, which shows the retention of expected mass spectral fragments with high LMSs when compared to a helium sourced library, such as NIST. Additionally, Figure 10 compares the extractor source (top) and HydroInert source (bottom) for a mixture of 68 SVOCs and PAHs when using H_2 carrier gas and shows excellent peak shape and improved peak shape for the HydroInert source compared to the extractor source.

A critical component of EPA 8270 is the tune criteria associated with the ion ratios of decafluorotriphenylphosphine (DFTPP). EPA method 8270 has been tested on the GC/MS/MS system, where the etune algorithm is used as the recommended tune (this has been noted in a previous application note).[5] For the GC/MS single quadrupole system, the DFTPP ion ratio criteria from Table 3 of EPA method 8270E and EPA method 8270D were used to test the HydroInert source with H_2 carrier gas.[3,4] 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 ng/µL, the method criteria, and if the measured relative abundances matched the criteria, where all measured relative abundances pass both the 8270E and 8270D ion ratio criteria.

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 helium to hydrogen carrier gas. Table 5 lists the RFs from EPA method 8270E Table 4 (guidance criteria), RFs from a GC/MS analysis with helium carrier gas, RFs for GC/MS analysis with HydroInert source and hydrogen carrier gas, and RFs for GC/MS/MS analysis with HydroInert source and hydrogen carrier gas. All test systems used 9 mm extraction lenses, respective of the source type (for example, the HydroInert source had a HydroInert 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 H_2 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 H_2 HydroInert GC/MS RF was 0.6. For the H_2 HydroInert GC/MS/MS analysis, there were 15 more compounds with RF values lower than the He GC/MS system, but the GC/MS/MS also opens the potential to analyze lower concentration levels down to 20 pg/µL, when the normal calibration range is 100 pg/µL to 100 ng/µL. In regards to sensitivity, 96 compounds were analyzed in a previous application for EPA 8270 with He carrier gas on GC/MS.[6] Comparing these compounds with the same set using the HydroInert source and H_2 carrier (also GC/MS), only five compounds had a smaller

Table 4. DFTPP ions, abundance criteria from EPA method 8270D and 8270E[3,4], 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*	11.4%	Pass
68	<2% of 69 *m/z*	1.7%	Pass
69	Present	27.2%	Pass
70	<2% of 69 *m/z*	1.0%	Pass
127	*10 to 80% of 198 *m/z*	31.1%	Pass
197	<2% of 198 *m/z*	0.1%	Pass
198	Base peak or present *or >50% of 442 *m/z*	73.7%	Pass
199	5 to 9% of 198 *m/z*	7.4%	Pass
275	10 to 60% of base peak	29.2%	Pass
365	>1% of base peak	3.5%	Pass
441	<150% of 443 *m/z* *present, but <24% of 442	86.4% *16.7%	Pass
442	Base peak or present *or >50% of 198 *m/z*	100% (base peak)	Pass
443	15 to 24% of 442 *m/z*	23.4%	Pass

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

Table 5. Response Factors (RFs) for select compounds from EPA method 8270E (Table 4 in the EPA method)[4], GC/MS single quadrupole analysis with He carrier gas, GC/MS single quadrupole analysis with Agilent HydroInert source and H_2 carrier gas, and GC/MS/MS tandem quadrupole analysis with HydroInert source and H_2 carrier gas.

Compound	Response Factor (RF) from EPA Method 8270E[4]	RF He GC/MS	RF H_2 HydroInert GC/MS	RF H_2 HydroInert GC/MS/MS
Acenaphthene	0.9	1.3	1.1	0.2
Acenaphthylene	0.9	1.9	1.4	0.1
Acetophenone	0.01	1.2	0.4	1.0
Anthracene	0.7	1.1	1.0	0.9
Benzo(a)anthracene	0.8	1.4	1.5	1.0
Benzo(a)pyrene	0.7	1.2	0.9	0.9
Benzo(b)fluoranthene	0.7	1.4	1.2	1.2
Benzo(g,h,i)perylene	0.5	1.1	1.0	1.3
Benzo(k)fluoranthene	0.7	1.2	1.2	1.3
Bis(2-chloroethoxy)methane	0.3	0.4	0.3	0.7
Bis(2-chloroethyl)ether	0.7	0.8	0.6	0.5
Bis-(2-ethylhexyl)phthalate	0.01	0.8	0.5	0.2
4-Bromophenyl-phenyl ether	0.1	0.3	0.2	0.2
Butyl benzyl phthalate	0.01	0.6	0.3	0.1
4-Chloroaniline	0.01	0.4	0.4	0.6
4-Chloro-3-methylphenol	0.2	0.3	0.2	0.4
2-Chloronaphthalene	0.8	2.4	1.0	0.8
2-Chlorophenol	0.8	0.8	0.7	0.5
4-Chlorophenyl-phenyl ether	0.4	0.7	0.5	0.3
Chrysene	0.7	1.2	1.1	0.4
Dibenz(a,h)anthracene	0.4	1.1	1.0	0.2
Dibenzofuran	0.8	1.7	1.5	1.4

linear range: hexachlorobutadiene, 2,6-dinitrotoluene, diethyl phthalate, 2,4-dinitrotoluene, and pentachlorophenol, where the first three were smaller by one concentration level, starting at 200 pg/µL instead of 100 pg/µL, and 2,4-dinitrotoluene calibration range was 0.1 to 75 ng/µL for the H_2 HydroInert analysis. The pentachlorophenol concentration range starts at 500 pg/µL with H_2 HydroInert GC/MS analysis, instead of 100 pg/µL. For benzoic acid, HydroInert with H_2 carrier gas exhibited the same calibration range from 0.8 to 100 ng/µL, as He carrier gas. H_2 carrier gas with the HydroInert source retains the sensitivity, for most of the semivolatile compounds tested are normally observed with He carrier gas.

Compound	Response Factor (RF) from EPA Method 8270E[4]	RF He GC/MS	RF H_2 HydroInert GC/MS	RF H_2 HydroInert GC/MS/MS
Di-*n*-butyl phthalate	0.01	1.3	0.8	0.8
3,3'-Dichlorobenzidine	0.01	0.5	0.4	0.1
2,4-Dichlorophenol	0.2	0.3	0.2	0.4
Diethyl phthalate	0.01	1.4	1.0	0.6
Dimethyl phthalate	0.01	1.4	1.0	0.8
2,4-Dimethylphenol	0.2	0.3	0.3	0.4
4,6-Dinitro-2-methylphenol	0.01	0.2	0.1	0.01
2,4-Dinitrophenol	0.01	0.2	0.1	0.02
2,4-Dinitrotoluene	0.2	0.4	0.2	0.03
2,6-Dinitrotoluene	0.2	0.3	0.2	0.03
Di-*n*-octyl phthalate	0.01	1.3	0.8	0.4
Fluoranthene	0.6	1.2	1.2	0.4
Fluorene	0.9	1.3	1.2	1.4
Hexachlorobenzene	0.1	0.3	0.3	0.4
Hexachlorobutadiene	0.01	0.2	0.2	0.4
Hexachlorocyclopentadiene	0.05	0.3	0.1	0.03
Hexachloroethane	0.3	0.2	0.1	0.14
Indeno(1,2,3-cd)pyrene	0.5	1.2	1.2	1.0
Isophorone	0.4	0.6	0.4	0.3
2-Methylnaphthalene	0.4	0.7	0.7	1.7
2-Methylphenol	0.7	0.7	0.6	0.5
4-Methylphenol	0.6	1.0	0.3	0.7
Naphthalene	0.7	1.1	1	0.9
2-Nitroaniline	0.01	0.4	0.23	0.05
3-Nitroaniline	0.01	0.3	0.18	0.03
4-Nitroaniline	0.01	0.3	0.21	0.13
Nitrobenzene	0.2	0.3	0.2	0.3
2-Nitrophenol	0.1	0.2	0.11	0.1
4-Nitrophenol	0.01	0.2	0.14	0.05
N-Nitroso-di-*n*-propylamine	0.5	0.4	0.4	0.03
N-Nitrosodiphenylamine	0.01	2.05	0.9	2.3
2,2'-Oxybis-(1-chloropropane)	0.01	0.45	0.54	0.03
Pentachlorophenol	0.05	0.18	0.1	0.1
Phenanthrene	0.7	1.2	1.1	1.1
Phenol	0.8	0.9	0.7	0.3
Pyrene	0.6	1.3	1.2	0.4
1,2,4,5-Tetrachlorobenzene	0.01	0.38	0.31	0.23
2,3,4,6-Tetrachlorophenol	0.01	0.36	0.17	0.07
2,4,5-Trichlorophenol	0.2	0.3	0.3	0.2
2,4,6-Trichlorophenol	0.2	0.3	0.2	0.2

As another example of the linear range retention, Figure 9 compares the linear range for nitrobenzene in He carrier gas (Figure 9A, top) and in H_2 carrier gas with HydroInert source (Figure 9B, bottom). The average RF RSD percentages are remarkably similar between the He and H_2 + HydroInert source results at 6.33% RSD for He and 6.59% RSD for H_2 carrier gas and HydroInert source.

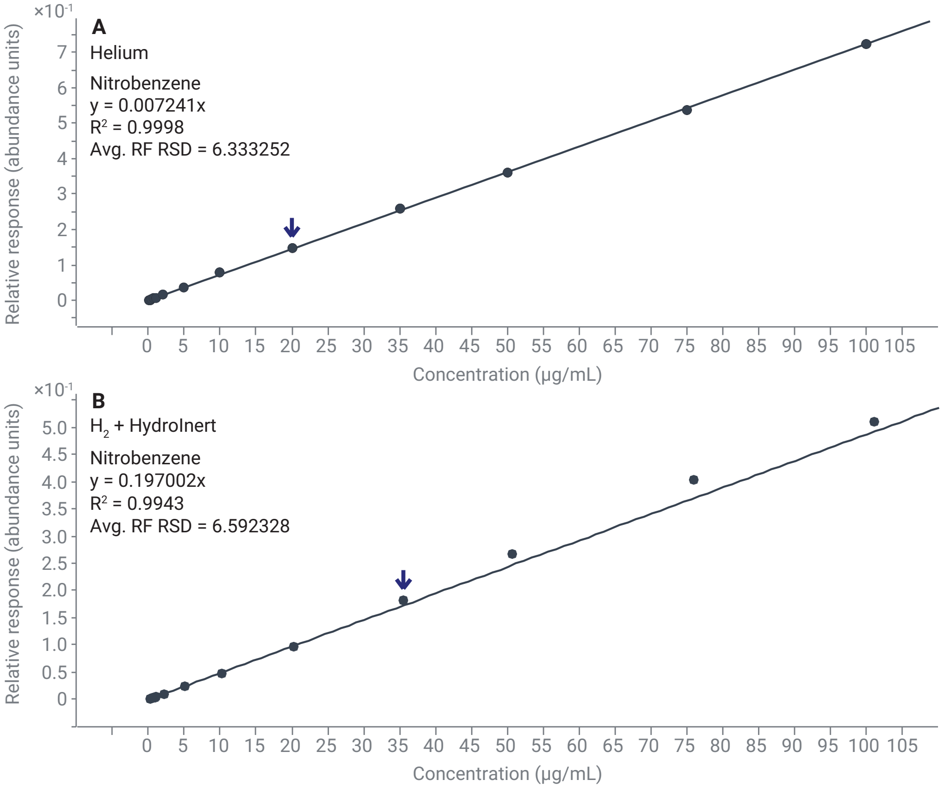


Figure 9. Nitrobenzene linear range (0.1 to 100 ng/µL) collected on a GC/MS system in (A) He and (B) H_2 carrier gas, with Agilent HydroInert source.

PAHs are a compound class that has been transitioned to H_2 analysis by GC/MS and GC/MS/MS, as they are very stable aromatic hydrocarbons.[7] They have also been tested with the HydroInert source. In using the HydroInert source with H_2 carrier gas, improved peak shape and resolution was observed when compared to an extractor source under the same method and carrier gas conditions, as shown in Figures 10 and 11. This was most visible with the later-eluting PAHs, such as benzo(b)fluoranthene, benzo(k) fluoranthene, and benzo(g,h,i)perylene (Figure 11).

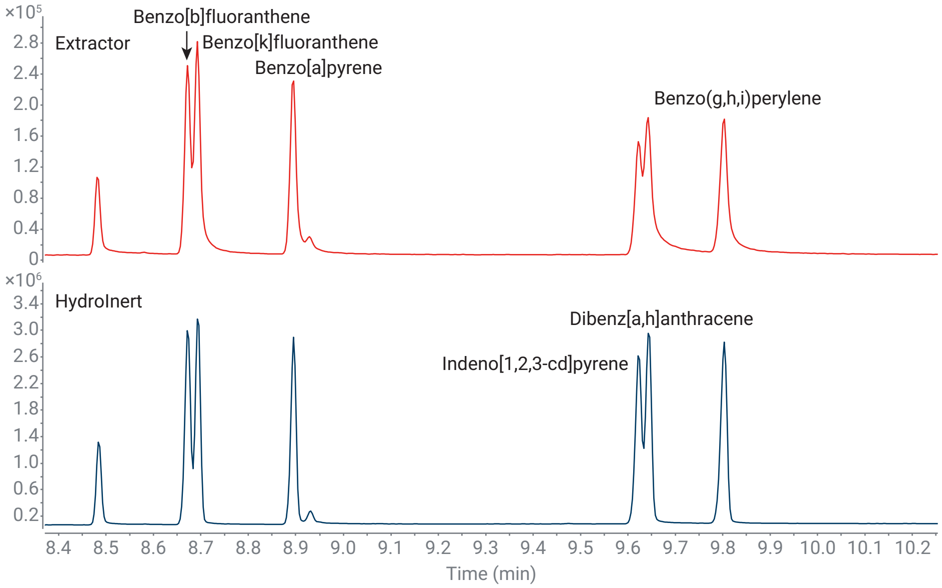


Figure 11. Zoom in of later-eluting PAH region to compare peak shape and resolution of these compounds when using H_2 carrier gas with an extractor source and Agilent HydroInert source at 50 ng/µL.

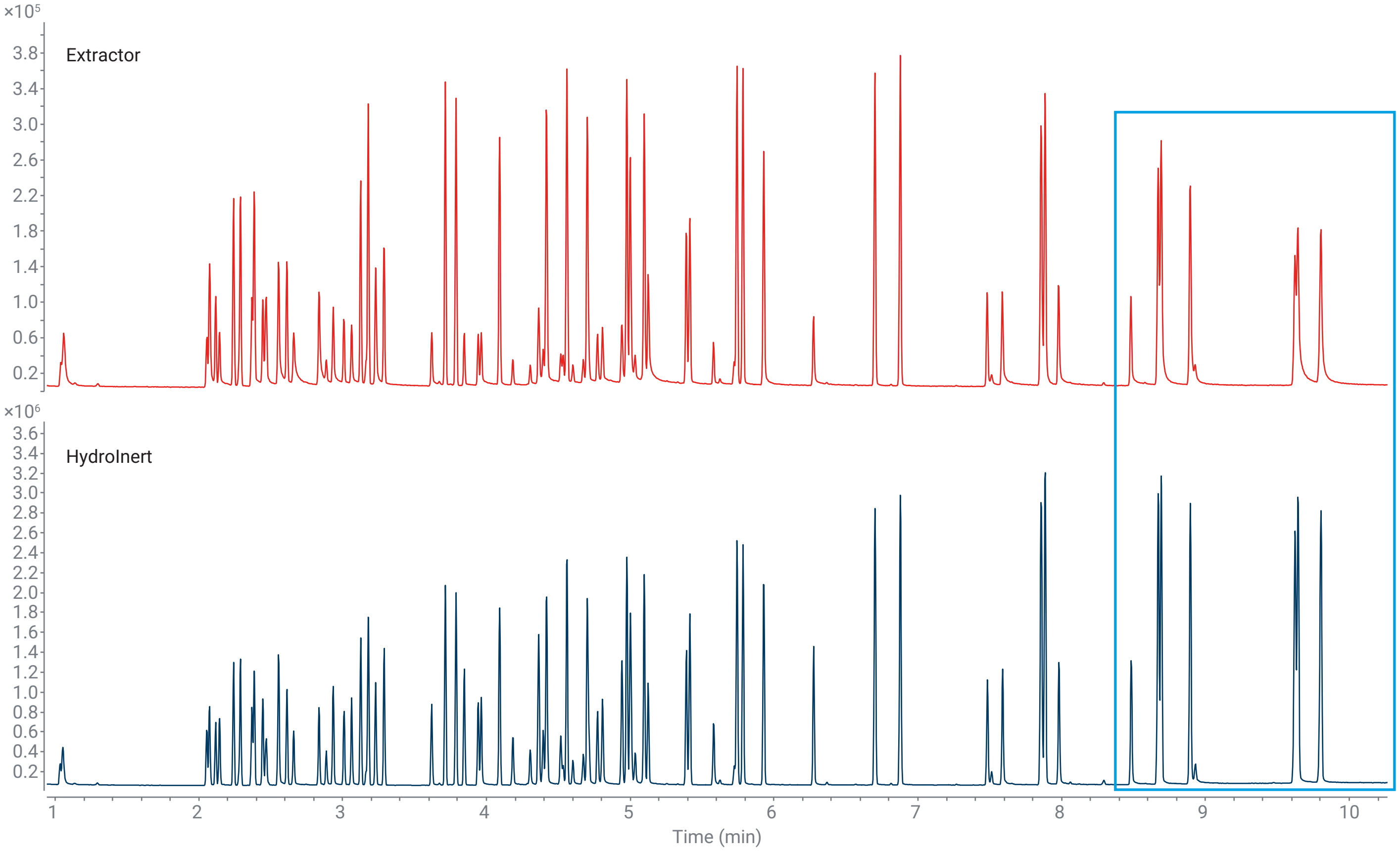


Figure 10. Comparison of peak shape and resolution for H_2 carrier gas with an extractor source and Agilent HydroInert source for a set of 68 target analytes for EPA method 8270 at 50 ng/µL.

Pesticide analysis

For pesticide analysis, a midcolumn backflush setup in an 8890 GC and 7000E triple quadrupole GC/MS was configured with two HP-5ms Ultra Inert GC columns 20 m × 0.18 mm, 0.18 µm, connected through an Agilent purged Ultimate union (PUU), H_2 carrier gas, and HydroInert source. This column set with H_2 carrier gas allowed the usage of the Agilent pesticide and environmental pollutants (P&EP) multiple reaction monitoring (MRM) database for retention times and MRM transitions, which was originally collected on a 15 × 15 m (0.25 mm × 0.25 µm) HP-5ms Ultra Inert GC column design with He carrier gas. The 20 × 20 m setup was retention-time locked. Multiple sets of pesticide standards were tested to evaluate the mass spectra of various compound classes commonly observed in pesticide analysis, like nitro compounds and heavily chlorinated compounds. Example pesticides from these mixtures include deltamethrin, ethalfluralin, fipronil, cyfluthrin, permethrin, captan, parathion, endrin, and heptachlor. The pesticide mixtures were tested with H_2 carrier gas using an Inert Plus source with a 3 mm extraction lens, the recommended lens for trace pesticide analysis in He, and using a HydroInert source with a 9 mm extraction lens. The first round of testing used scan mode for acquisition to understand if the fragmentation profiles were retained for various pesticides with H_2 carrier gas, if ion abundances changes, or new hydrogenation product ions were identified in both source cases. Ethalfluralin contains two nitro groups and a change in the most abundant ions are viewed best when overlaying the top five EICs; the comparison of sources is shown in Figure 12. The five highest abundance ions for ethalfluralin, from helium collected mass spectrum, are 55, 276, 56, 316, and 292 *m/z*. If the nitro groups become hydrogenated in the

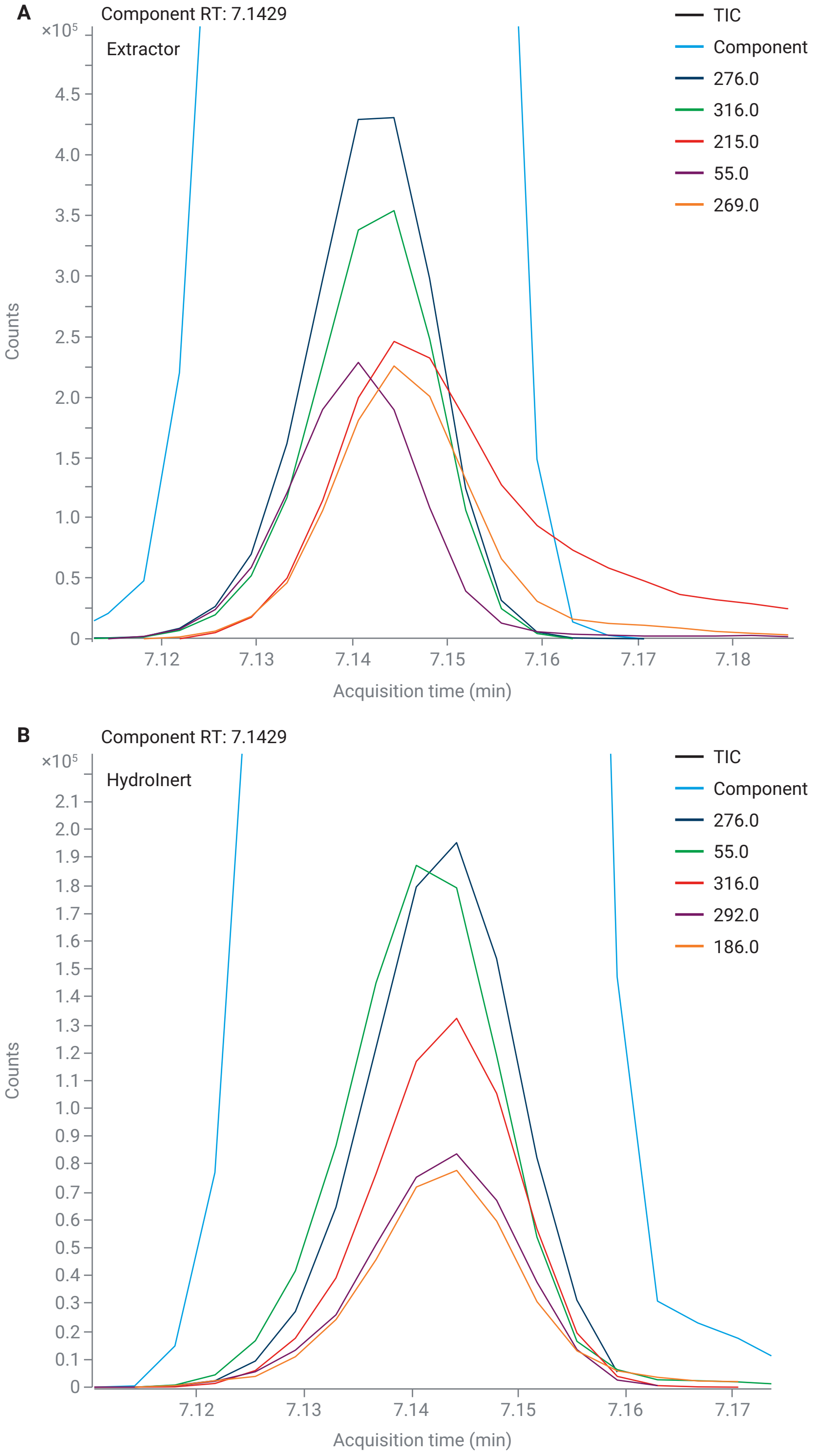


Figure 12. EICs of the top five abundant ions for ethalfluralin with H_2 carrier gas and (A) extractor source with 3 mm extraction lens and (B) Agilent HydroInert source with 9 mm extraction lens.

source, the mass spectrum would have a significant contribution of 269 *m/z*, which is not a significant ion in the reference He mass spectrum. For H_2 carrier gas with extractor source (Inert Plus), Figure 12A shows the top five abundant ions, which include 269 and 215 *m/z*, and indicate hydrogenation in the source; there is also rearrangement in the most abundant ions, where 55 *m/z* is suppressed to the fourth most abundant with an increase in 316 *m/z* ranking and inclusion of 215 *m/z*, which is a small contribution in the normal He spectra. Comparatively, Figure 12B of the same experiment with the HydroInert source has no 269 *m/z* in the top five abundant ions, indicating no hydrogenation. Retention of expected ion abundance with the HydroInert source in presence of H_2 allows method developers to use the same MRM transitions or selected ion monitoring (SIM) ions and would require less time in a transition to hydrogen carrier gas.

Another example of differences between the extractor source and HydroInert source with H_2 carrier gas is observed with deltamethrin. Deltamethrin is one of the pesticide compounds with a cyano(4-phenoxyphenyl)methyl-2,2-dimethylcyclopropanecarboxylate structure; compounds in this class have different functional groups after the cyclopropane structure. These compounds also share a cleavage point at the C–O bond of the ester group with a major fragment associated with 209 *m/z*, an *m*-phenoxyphenylacetonitrile structure. This 209 *m/z* fragment typically appears in deltamethrin mass spectrum, but at lower abundance. The deltamethrin results from scan acquisition were reviewed in MassHunter Unknowns Analysis software, and in some cases, deltamethrin was not identified at the typical retention time of 18.17 minutes with the extractor source. Instead, *m*-phenoxyphenylacetonitrile was identified, as shown in Figure 13A, with a large abundance of 209 *m/z* and no ion abundance at 253 *m/z*. In some other runs with the extractor source, deltamethrin was identified (Figure 13B), but with LMSs in the 70s range and large abundance of 209 *m/z*. In Figure 13C, deltamethrin was identified with LMS values between 91 and 94 and the deconvoluted mass spectrum is remarkably similar to the (He) NIST library spectrum on the bottom.

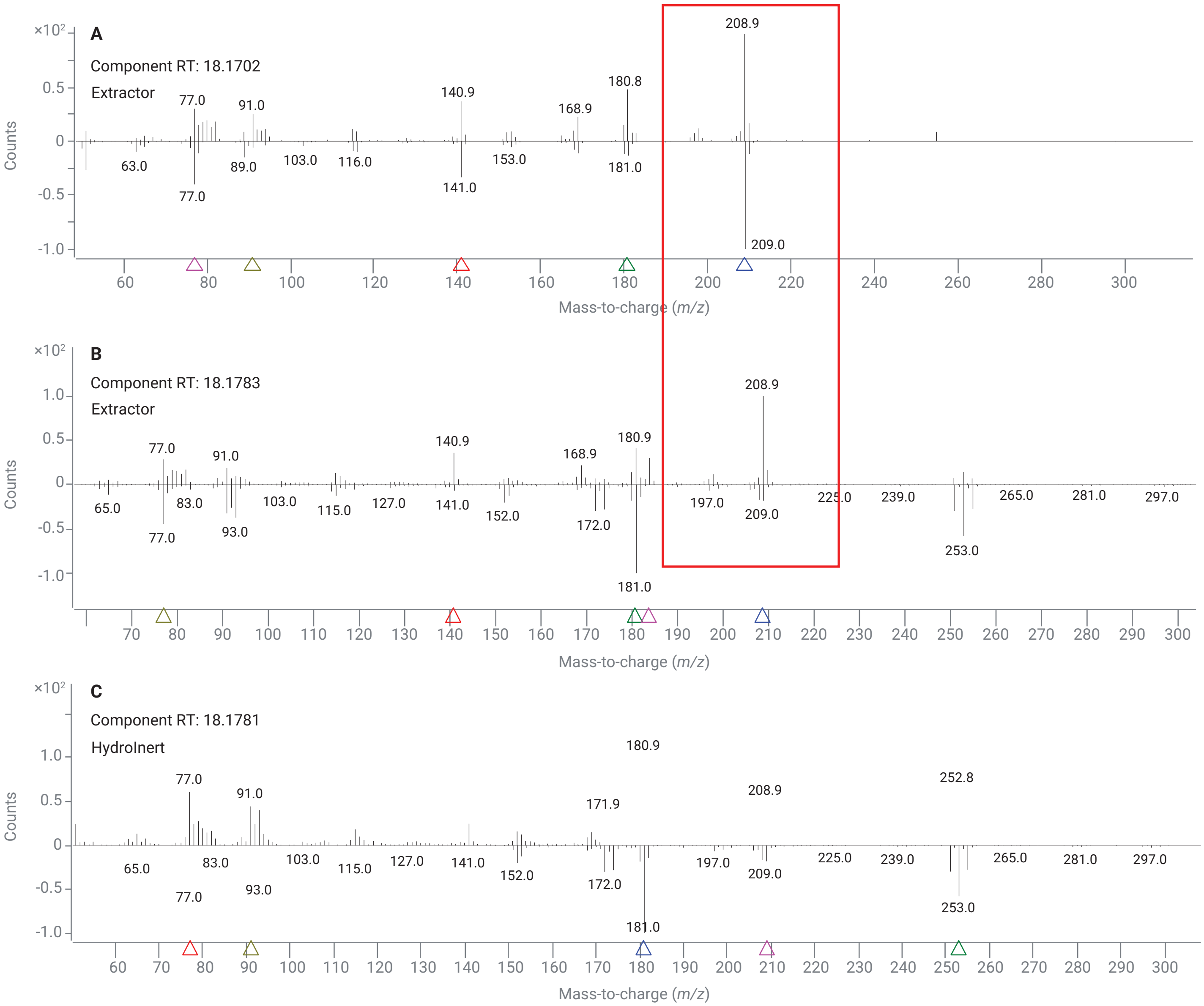


Figure 13. Head-to-tail comparison of deconvoluted mass spectrum (top of each subfigure) to library mass spectrum, NIST17.L (bottom of each subfigure) for deltamethrin with H_2 carrier gas and (A) extractor source with 3 mm extraction lens run 1, (B) extractor source with 3 mm extraction lens run 2, and C) Agilent HydroInert source with 9 mm extraction lens.

Volatile organic compounds (VOCs)

For VOCs, a 6 mm HydroInert extraction lens is recommended, but a 9 mm HydroInert extraction lens may also be an option. A method was developed for rapid identification and quantification of volatiles at low µg/L levels in water samples. The combination of the Agilent 8697 headspace sampler, 8890 GC, and 5977C GC/MSD, when using H_2 carrier gas and the new HydroInert EI source, provides this capability for many volatiles in water.

The headspace approach often provides a simpler alternative to purge and trap sampling, if local regulations allow it. The data in Figure 14 was run in scan mode for broad screening with spectral confirmation, as it is possible to measure lower levels with SIM acquisition of selected targets. The identification of the four trihalomethanes with their expected most abundant ions displays the ability of the HydroInert source to prevent dehalogenation in the presence of H_2 carrier gas. Additionally, Table 6 tabulates the LMSs from comparing the deconvoluted spectra to the NIST library.

The match scores of 80 and higher indicate excellent retention of the normal fragmentation pattern in H_2 carrier gas with the HydroInert source, when compared to NIST library mass spectra, which were collected with He.

Table 6. NIST helium library scores for select low-level (µg/L) trihalomethanes analyzed with H_2 carrier gas and the Agilent HydroInert source.

	Retention Time (minutes)	NIST LMS
Trichloromethane	2.107	93
Bromodichloromethane	2.792	86
Dibromochloromethane	3.526	88
Tribromomethane	4.267	80

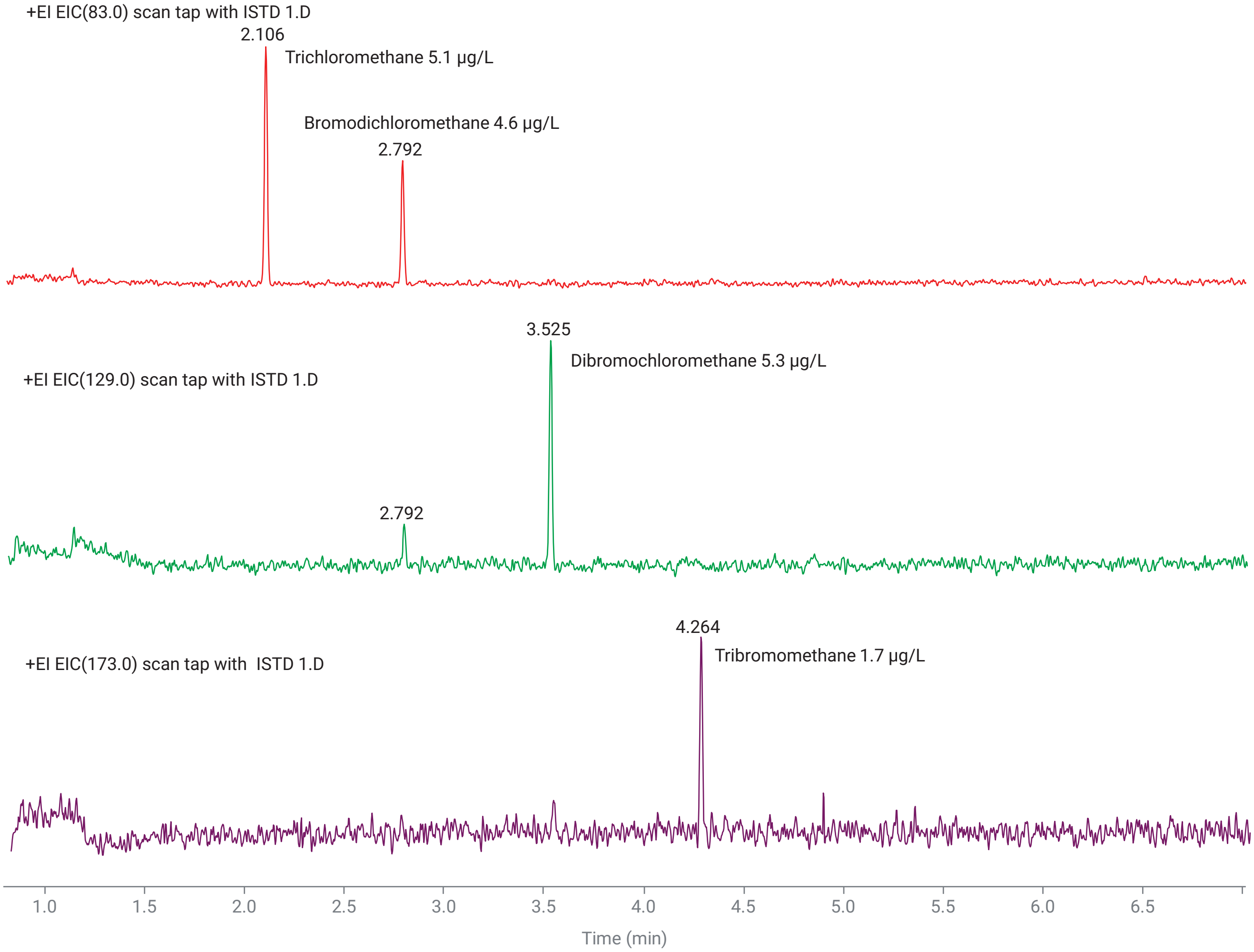


Figure 14. Extracted ion chromatograms (EICs) of 83, 129, and 173 *m/z* with identification and quantification of four trihalomethanes when running a headspace HS/GC/MS system with H_2 carrier gas and the Agilent HydroInert source.

HydroInert upgrade kits and complete source assembly

Figure 15 is a broken-out parts diagram of an assembled HydroInert source, with the HydroInert-specific parts highlighted in a purple color (parts 17, 12, 3, 4, 10, and 9, if looking from left to right of the figure). Additionally, item number 16, source heater block assembly, is specialized for the HydroInert source with "H_2" etched into the face to indicate that the HydroInert source, which is compatible with H_2 carrier gas, is currently installed into a mass spectrometer. All other parts in the diagram are the same as found in an Inert Plus (or extractor) source. Table 7 contains the parts associated with each number in Figure 15. Parts 11, 13, 14, and 15 are inserted into the front of the heater block and not shown individually in this figure.

HydroInert complete source assembly (part number G7078-67930) and HydroInert GC/MSD upgrade kit (part number 5505-0083) for the existing Agilent 5977A extractor GC/MSD and Agilent 5977B Inert Plus GC/MSD are available. The fully assembled source is ready to install into the mass spectrometer without having to change out parts of an existing source, which would be required with the HydroInert GC/MSD upgrade kit. All the parts listed in Table 8 are included in the HydroInert GC/MSD upgrade kit. The HydroInert source is not compatible with older mass spectrometer models, such as the Agilent 5975 Series GC/MSD, nor with stainless steel or inert sources.

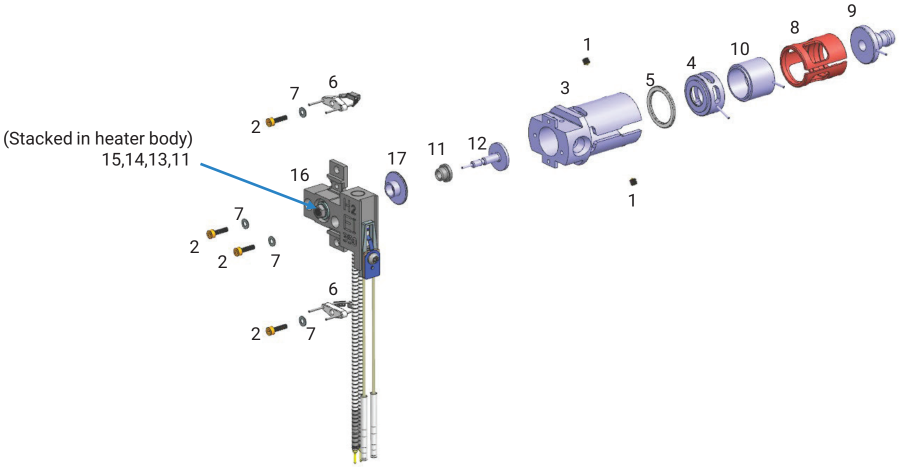


Figure 15. Broken-out parts of an assembled Agilent HydroInert source.

Table 7. List of parts in a fully assembled Agilent HydroInert source for an Agilent Inert Plus GC/MS system.

Item Number (Figure 15)	Part Name	Part Number
1	Setscrews	G3870-20446
2	Screws	G3870-20021
3	Extractor source body*	G7078-20903
4	Extractor lens–9 mm*	G7078-20909
5	Extractor lens insulator	G3870-20445
6	Filament	G7005-60061
7	Spring washer Flat washer	3050-1301 3050-0982
8	Lens insulator	G3870-20530
9	Entrance lens*	G7078-20904
10	Ion focus lens*	G7078-20905
11	Repeller insulator	G1099-20133
12	Repeller*	G7078-20902
13	Flat washer	3050-0891
14	Belleville spring washer	3050-1301
15	Repeller nut	0535-0071
16	H_2 EI heater/sensor assembly*	G7078-67910
17	Insert*	G7078-20901

* HydroInert-specific parts.

The HydroInert complete source assembly (part number G7006-67930) and HydroInert triple quadrupole GC/MS upgrade kit (part number 5505-0084) for the existing Agilent 7000C/D triple quadrupole GC/ MS systems are available. All the parts listed in Table 9 are included in the HydroInert triple quadrupole GC/MS upgrade kit. If a user already has a 7000C or 7000D Inert Plus triple quadrupole GC/MS, a HydroInert triple quadrupole GC/MS upgrade kit could be purchased that includes the HydroInert mass spectrometer parts indicated in Figure 15, except the entrance lens is an extended entrance lens, which is designed specifically for the tandem quadrupole systems.

If multiple sources are kept in the laboratory, the HydroInert parts should be stored separately from other sources and kept with the H_2 heater/sensor assembly for easy identification that an H_2-compatible (HydroInert) source is installed in the MS system. Additionally, the triple quadrupole parts should be kept separate from the single quadrupole parts as the entrance lenses are different lengths and should not be swapped.

Table 8. Agilent HydroInert GC/MSD upgrade kit for the Agilent 5977A extractor GC/MSD, Agilent 5977B Inert Plus GC/MSD or Agilent 5977C GC/MSD) with part numbers and item number indicated in Figure 15.

Item Number (Figure 15)	Part Name	Part Number
NA	HydroInert GC/MSD upgrade	5505-0083
17	Insert*	G7078-20901
12	Repeller*	G7078-20902
3	Extractor source body*	G7078-20903
9	Entrance lens*	G7078-20904
10	Ion focus lens*	G7078-20905
4	Extractor lens– 9mm*	G7078-20909
16	H_2 EI heater/sensor assembly*	G7078-67910
NA	Wire, extractor lens	G7000-60827
11	Repeller insulator (x2)	G1099-20133

* HydroInert-specific parts.

Table 9. Agilent HydroInert triple quadrupole GC/MS upgrade kit for the Agilent 7000C/D/E triple quadrupole mass spectrometers, with part numbers and item numbers indicated in Figure 15.

Item Number (Figure 15)	Part Name	Part Number
NA	HydroInert GC/TQ upgrade	5505-0084
17	Insert*	G7078-20901
12	Repeller*	G7078-20902
3	Extractor source body*	G7078-20903
9**	Entrance lens –extended*, **	G7006-60926
10	Ion focus lens*	G7078-20905
4	Extractor lens–9 mm*	G7078-20909
16	H_2 EI heater/sensor assembly*	G7078-67920
NA	Wire, extractor lens	G7000-60827
11	Repeller insulator (x2)	G1099-20133

* HydroInert-specific parts.

** The extended entrance lens for the HydroInert MS/MS system is longer than the entrance lens of a single quadrupole MS system.

Before installing the HydroInert ion source, verify that the instrument hardware supports use of this source. The HydroInert ion source is supported on:

- 5977 Series GC/MSD Single Quad instrument models 5977A, 5977B, and 5977C
- 7000 Series GC/TQ Triple Quad instrument models 7000C, 7000D, and 7000E

Note: Diffusion pump single quadrupole instruments are not supported. A turbo pump is required.

For systems that are purchased with either the HydroInert ion source or Extractor (Inert Plus) ion source installed, all components necessary to use the HydroInert are already installed.

For systems sold before the introduction of the HydroInert source that are not already using these components, such as 5977 series instruments using a stainless steel or inert ion source, it will be necessary to install these components before using the HydroInert ion source.

These components include:

- A transfer line tip seal to electrically isolate the ion source from the transfer line
- Two wires that connect from the ceramic ion source board to the ion source
- A green wire to control the voltage of the ion source body
- A brown wire to control the voltage of the extractor lens

If you need assistance with method development and optimization, the Agilent global team of experts can help with your application needs through the Agilent CrossLab Application Services, in Method and Application Services (part number H2149A; R1736A) or Method Optimization (part number R1736C; R-21H-501).

Conclusion

The Agilent HydroInert source with H_2 carrier gas provides a more sustainable alternative to He carrier gas, and helps improve performance of H_2 carrier gas for GC/MS and GC/MS/MS analyses. The novel source comes fully assembled or as part of an upgrade kit for existing GC/MS and GC/MS/MS systems. In terms of performance, the HydroInert source retains mass spectral fidelity and allows users to continue using existing helium-based mass spectral libraries.

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Application Note

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Optimized PAH Analysis Using Triple Quadrupole GC/MS with Hydrogen Carrier

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Abstract

The Agilent 8890/7000D triple quadrupole GC/MS system with hydrogen carrier gas was used for the analysis of polycyclic aromatic hydrocarbons (PAHs). Optimized system performance with hydrogen carrier over an extended calibration range was achieved by carefully selecting instrument configuration and operating conditions. With the appropriate choice of column dimensions, liner, collision cell gas flow, collision energies, high-purity hydrogen, and an alternative drawout lens, excellent linearity across a calibration range of 0.1 to 1,000 pg was demonstrated.

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Introduction

PAHs are a group of chemical compounds that are composed of at least two or more fused conjugated benzene rings with a pair of carbon atoms shared between rings in their molecules. Because PAHs originate from multiple sources, they are widely distributed as contaminants throughout the world. Given their ubiquitous nature, they are monitored as trace contaminants in many different food products ranging from seafood to edible oils to smoked meats. They are also monitored in the environment including in air, water, and soil. PAHs have been analyzed by multiple techniques including HPLC/UV, GC/FID, GC/MS, or GC/TQ.

This application note focuses on GC/TQ in multiple reaction monitoring (MRM) mode using hydrogen as the GC carrier gas. While helium is the best carrier gas for GC/MS analysis, its reoccurring shortages have increased demand for applications using hydrogen as the carrier gas. When adopting hydrogen for GC/MS analysis, there are several things to consider.

First, hydrogen is a reactive gas, and may potentially cause chemical reactions in the inlet, column, and sometimes the mass spectrometer electron ionization (EI) source that can change analysis results. It is important to ensure there are no chemical reaction problems between analytes and hydrogen gas at elevated temperatures in the GC/MS.

Second, it is essential to use a reliable source of clean hydrogen gas. For long-term use, generators with a >99.9999% specification and low individual specs on water and oxygen are recommended. Moisture filters are recommended for use with hydrogen generators. For short-term use, cylinders with chromatographic or research-grade hydrogen are acceptable. It is also recommended that anyone working with flammable or explosive gases take a lab safety course covering proper gas handling and use.

Additionally, for GC/MS applications, hardware changes in the gas chromatograph and mass spectrometer are required when switching to hydrogen carrier gas.[1] This includes the inlet liner, column, vacuum pump, and EI drawout lens selection. Chromatographic conditions and injection solvent also need to be adjusted.

One of the advantages observed with hydrogen carrier gas is a reduced need for EI source cleaning. A similar improvement is observed when using Agilent JetClean technology, which uses a low continuous flow of hydrogen into the source during the analysis.[2]

PAHs are relatively durable compounds that do not exhibit high reactivity with hydrogen at the temperatures used in GC/MS analysis. Analysis of PAHs can therefore be performed with hydrogen carrier gas when using the optimized method and following the recommendations described in this application note. Other challenges with PAH analysis addressed in this work include peak tailing, often seen for late eluting analytes, and ISTD response inconsistency across the calibration range. With the optimized method, excellent linearity of R^2 >0.999 was observed for 24 of 27 analytes over 0.1 to 1,000 pg calibration range, and R^2 >0.996 for 26 analytes over the same range. For acenaphthylene, calibration was performed between 0.25 and 1,000 pg, with R^2 = 0.9999.

Experimental

The system used in this experiment was configured to minimize the potential problems with hydrogen carrier gas in PAH analysis. The important techniques used were:

- **Hydrogen gas:** In-house hydrogen with 99.9999% purity specification and low individual specs on water and oxygen was used as a carrier gas.
- **Pulsed splitless injection:** Used to maximize transfer of the PAHs, especially the heavy ones, into the column.
- **Column dimensions:** A DB-EUPAH column (20 m × 0.18 mm id, 0.14 µm) was used to maintain optimal gas flow and inlet pressure.
- **Collision gas:** Only nitrogen should be used as collision gas in GC/TQ when hydrogen is the carrier gas. The collision cell helium inlet fitting must be capped. The optimal nitrogen gas flow was shown to be 1.5 mL/min (Figure 1), which agreed with the user manual recommendation.
- **MS/MS:** The added selectivity of MRM mode in GC/TQ simplifies the data review of high matrix samples relative to GC/MS by reducing or eliminating interfering responses from the matrix.[3] Interfering responses often require manual integration of quantifier or qualifier ions.

- **Optimizer for GC/TQ:** The new optimizer software in Agilent MassHunter (MH) Acquisition 10 was used to determine the best collision energies for use with hydrogen carrier gas. With the *start with MRMs* workflow, the collision energies for the imported helium MRM transitions were optimized over two injections with no manual intervention. The re-optimized collision energies are shown in Table 1.

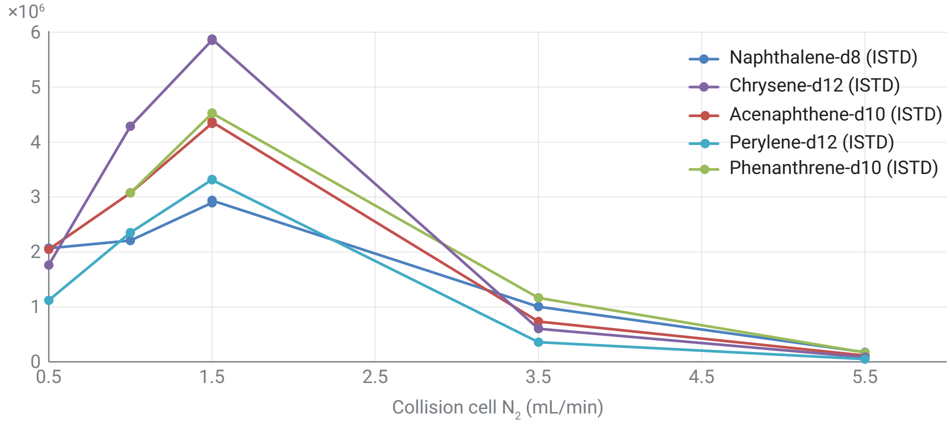


Figure 1. Absolute ISTD area response plotted versus collision cell nitrogen flow.

Table 1. MRM transitions used for quantifier and qualifiers with collision energies optimized for hydrogen carrier gas.

Name	RT	Quantifier	Collision Energy, Helium Carrier	Collision Energy, Hydrogen Carrier	Qualifier	Collision Energy, Helium Carrier	Collision Energy, Hydrogen Carrier
Napthalene-d8 (ISTD)	4.5768	136.0 → 136.0	19	25			
Napthalene	4.599	128.0 → 102.0	22	20	128.0 → 127.0	20	20
1-methylnaphthalene	5.1946	142.0 → 115.0	30	35	142.0 → 141.0	30	20
2-methylnaphthalene	5.3493	142.0 → 115.0	30	30	142.0 → 141.0	30	20
Biphenyl	5.7227	154.0 → 152.0	25	30	154.0 → 153.0	25	20
2,6-dimethylnaphthalene	5.7501	156.0 → 115.0	30	35	156.0 → 141.0	30	20
Acenapthylene	6.2923	152.0 → 151.0	40	20	152.0 → 150.0	40	35
Acenaphthene-d10 (ISTD)	6.3823	162.0 → 160.0	19	30			
Acenapthene	6.4221	154.0 → 152.0	40	35	153.0 → 152.0	40	40
2,3,5-trimethylnaphthalene	6.6007	170.0 → 155.0	25	20	170.0 → 153.0	25	30
Fluorene	6.933	166.0 → 165.0	30	25	166.0 → 163.0	34	50
Dibenzothiophene	8.1912	184.0 → 139.0	40	40	184.0 → 152.0	40	25
Phenanthrene-d10 (ISTD)	8.3459	188.0 → 188.0	19	25			
Phenanthrene	8.3881	178.0 → 176.0	34	35	178.0 → 152.0	30	30
Anthracene	8.4356	178.0 → 152.0	30	25	178.0 → 176.0	34	35
1-methylphenanthrene	9.4398	192.0 → 191.0	25	20	192.0 → 165.0	30	40
Fluoranthene	10.8	202.0 → 200.0	50	40	202.0 → 201.0	50	25
Pyrene	11.474	202.0 → 200.0	50	40	202.0 → 201.0	30	30
Benzo(a)anthracene	14.657	228.0 → 226.0	38	35	228.0 → 224.0	38	55
Chrysene-d12 (ISTD)	14.809	240.0 → 236.0	25	40	118.0 → 116.0	25	20
Chrysene	14.892	228.0 → 226.0	38	35	228.0 → 224.0	38	55
Benzo(b)fluoranthrene	17.738	252.0 → 250.0	42	40	250.0 → 248.0	40	40
Benzo(k)fluoranthrene	17.803	252.0 → 250.0	42	40	250.0 → 248.0	40	40
Benzo(j)fluoranthrene	17.886	252.0 → 250.0	42	40	250.0 → 248.0	40	45
Benzo(e)pyrene	18.696	252.0 → 250.0	40	40	250.0 → 248.0	40	45
Benzo(a)pyrene	18.833	252.0 → 250.0	40	40	250.0 → 248.0	40	40
Perylene-d12 (ISTD)	19.084	264.0 → 260.0	40	45	264.0 → 236.0	25	35
Perylene	19.156	252.0 → 250.0	40	40	250.0 → 248.0	40	45
Dibenz(a,c)anthracene	21.45	278.0 → 276.0	38	40	276.0 → 274.0	38	40
Indeno(1,2,3,-cd)pyrene	21.501	276.0 → 274.0	42	42	138.0 → 124.0	42	42
Dibenz(a,h)anthracene	21.536	278.0 → 276.0	42	42	278.0 → 272.0	60	60
Benzo(g,h,i)perylene	22.258	276.0 → 274.0	42	42	274.0 → 272.0	45	45

- **9 mm Extractor lens:** The standard 3 mm extractor (drawout) lens provided with the 7000D GC/TQ is a good choice for general analysis with helium carrier gas. However, the optional 9 mm lens is recommended when using hydrogen as a carrier gas in GC/MS analysis. Additionally, with the propensity of PAHs to deposit on surfaces, it has been found that the 9 mm lens provides better calibration linearity, ISTD response consistency, precision of response, and peak shape.[4,5]

Figure 2 shows the system configuration used for the experimental work.

The instrument operating parameters are listed in Tables 1 and 2. Instrument temperatures must be kept high enough to prevent deposition of the highest boiling PAHs onto flow path components. The inlet and MSD transfer line are maintained at 320 °C. The MS source should be a minimum of 320 °C.

PAH calibration standards were diluted from the Agilent PAH Analyzer calibration kit (part number G3440-85009) using isooctane. The kit contains a stock solution of 27 PAHs at 10 µg/mL and a stock solution of five ISTDs at 50 µg/mL. Twelve calibration levels were prepared: 0.1, 0.25, 0.5, 1, 2, 10, 20, 100, 200, 400, 750, and 1,000 pg/µL. Each level also contained 500 pg/µL of the ISTDs. See Table 1 and Figure 2 for compound identifications.

When using hydrogen as a carrier gas, laboratory safety considerations must be observed. The Agilent 8890 Gas Chromatograph Safety Manual and the operation manual for the instrument contain hydrogen safety instructions. It is also recommended that anyone working with flammable or explosive gases take a lab safety course covering proper gas handling and use.

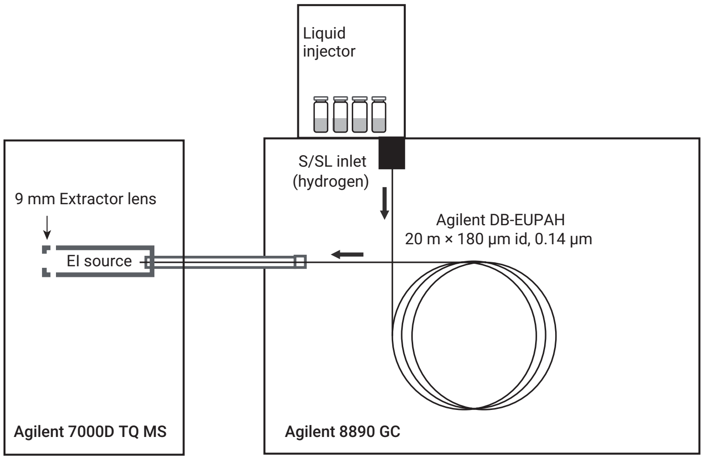


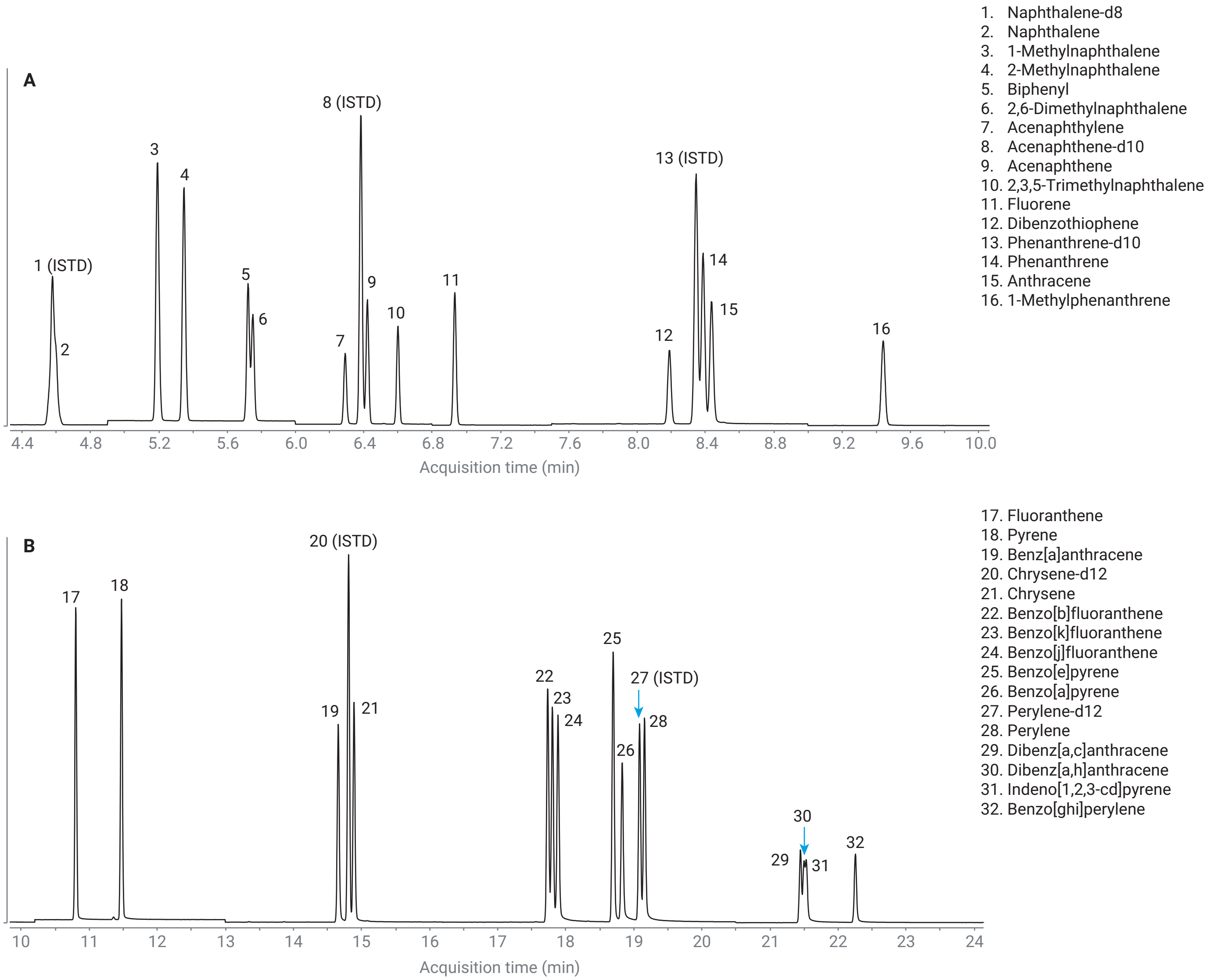
Figure 2. The Agilent 8890/7000D GC/TQ system configuration.

Table 2. Gas chromatograph and mass spectrometer conditions for PAH analysis.

Agilent 8890 GC with Fast Oven, Autoinjector, and Tray	
Inlet	EPC split/splitless
Mode	Pulsed splitless
Injection Pulse Pressure	40 psi until 0.75 min
Purge Flow To Split Vent	50 mL/min at 0.70 min
Septum Purge Flow Mode	Standard, 3mL/min
Injection Volume	1.0 µL
Inlet Temperature	320 °C
Carrier Gas	Hydrogen
Inlet Liner	Agilent universal low pressure drop, with glass wool (p/n 5190-2295)
Oven	Hold 60 °C for 1 min; 25 °C/min to 200 °C; 8 °C/min to 335 °C; Hold for 6.325 min
Total Run Time	29 min
Post Run Time	0
Equilibration Time	0.5 min
Column	Agilent DB-EUPAH, 20 m × 0.18 mm, 0.14 µm (p/n 121-9627)
Control Mode	Constant flow
Flow	0.648 mL/min
Initial Inlet Pressure	4.8463 psig
Inlet Connection	Split/splitless
Agilent 7000D TQ MS	
Source	Inert extractor
Drawout Lens	9 mm
Tune File	atunes.eiex.tune.xml
Mode	MRM
Collision Gas	Nitrogen, 1.5 mL/min
Solvent Delay	3.5 min
EM Voltage Gain Mode	10
Quad Temperature	150 °C
Source Temperature	325 °C
Transfer line Temperature	320 °C

Results and discussion

Figure 3 shows the MRM TIC of the 100 pg/µL PAH calibration standard with the ISTDs present at 500 pg/µL. The chromatograms show the high chromatographic resolution achieved with hydrogen under the analysis conditions. Peak tailing is commonly seen on the later eluting analytes, which would require manual integration and prolonged data review. With the instrument parameters and analysis conditions chosen here, the peak shapes for all PAHs, even the latest eluting ones, are very good.



1. Naphthalene-d8
2. Naphthalene
3. 1-Methylnaphthalene
4. 2-Methylnaphthalene
5. Biphenyl
6. 2,6-Dimethylnaphthalene
7. Acenaphthylene
8. Acenaphthene-d10
9. Acenaphthene
10. 2,3,5-Trimethylnaphthalene
11. Fluorene
12. Dibenzothiophene
13. Phenanthrene-d10
14. Phenanthrene
15. Anthracene
16. 1-Methylphenanthrene

17. Fluoranthene
18. Pyrene
19. Benz[a]anthracene
20. Chrysene-d12
21. Chrysene
22. Benzo[b]fluoranthene
23. Benzo[k]fluoranthene
24. Benzo[j]fluoranthene
25. Benzo[e]pyrene
26. Benzo[a]pyrene
27. Perylene-d12
28. Perylene
29. Dibenz[a,c]anthracene
30. Dibenz[a,h]anthracene
31. Indeno[1,2,3-cd]pyrene
32. Benzo[ghi]perylene

Figure 3. The MRM TIC of the 100 pg/µL calibration standard with 500 pg/µL ISTDs.

With the DB-EUPAH GC column and oven temperature program ramp described in the experimental section, near baseline separation was achieved for benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(j)fluoranthene, shown in Figure 4. The resolution was maintained throughout the calibration range and the MRM chromatograms for the quantifier and qualifier ions are shown for 0.1 pg/µL (lowest calibration standard), 1 pg/µL, and 100 pg/µL. Total analysis time was 29 minutes, with the latest target analyte eluting before 23 minutes. A faster oven temperature ramp will shorten run time and can be used if extra resolution is not needed.

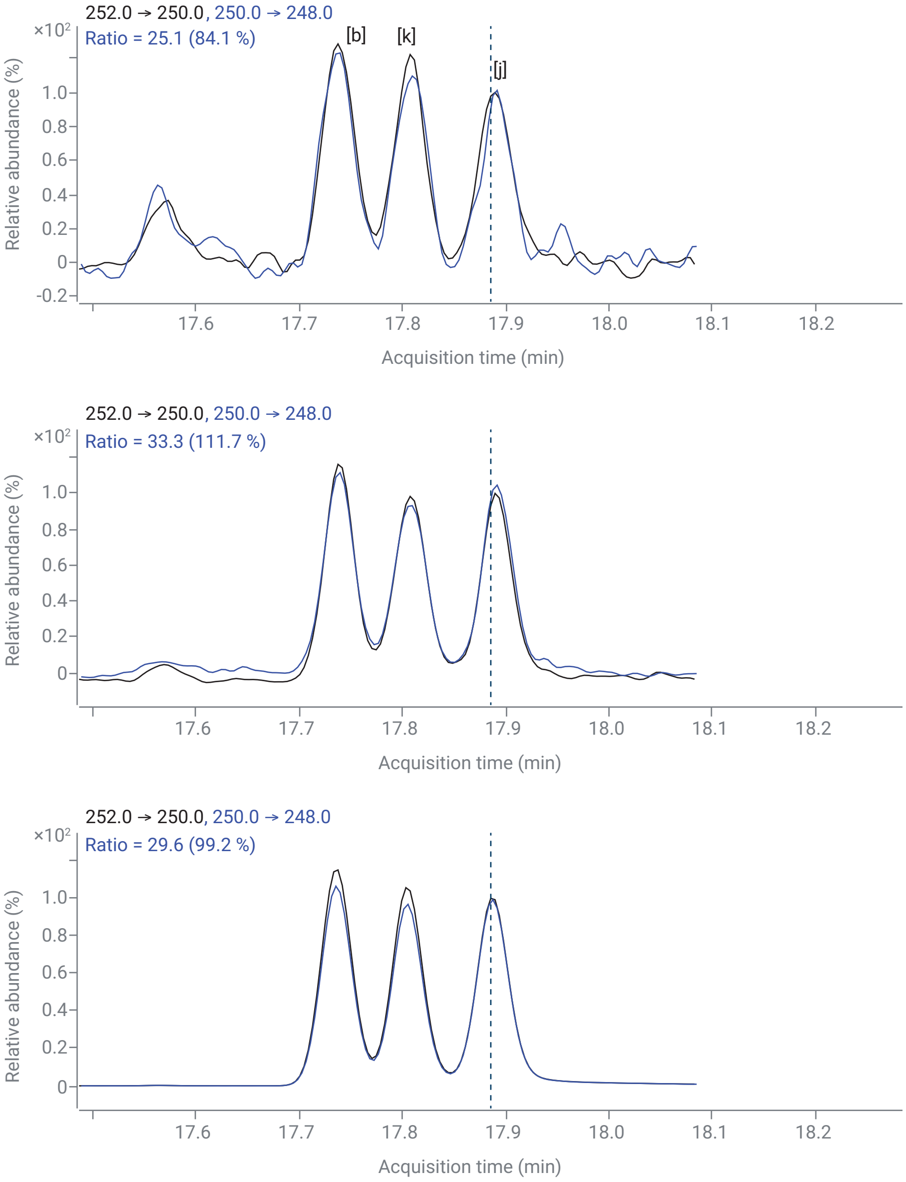


Figure 4. Response at quantifier and qualifier MRM transitions for benzo(b)fluoranthene, benzo(k) fluoranthene, and benzo(j)fluoranthene at 0.1 pg (the lowest calibration level), 1 pg, and 100 pg.

The use of hydrogen carrier gas typically results in a slightly reduced signal-to-noise ratio (S/N), so it is important to check the lowest desired calibration level. Table 3 shows the S/N of the quantifier ion for the target PAH analytes at 0.1 pg. For 26 out of 27 targets, S/N >3 was observed at 0.1 pg. For acenaphthylene, the lowest limit of calibration was increased to 0.25 pg to achieve S/N >3.

Excellent linearity with R^2 >0.999 was observed for 24 out of 27 analytes over the calibration range 0.1 to 1,000 pg and R^2 >0.996 for 26 analytes over the same range. For acenaphthylene, calibration was performed between 0.25 and 1,000 pg, with R^2 = 0.9999. Quantitation accuracy was maintained throughout the calibration range. As an example, accuracy at 100 pg is shown in Table 3. It is within ±4% for 26 out of 27 targets, and dibenz(a,h)anthracene was quantified within ±9% of its target concentration.

Table 3. R^2 values of 12-level ISTD calibration 0.1 to 1,000 pg MRM, S/N at the lowest calibration level of 0.1 pg, and quantitation accuracy at 100 pg.

Name	RT	CF Limit Low (pg)	CF Limit High (pg)	CF R^2	S/N at 0.1 pg	Accuracy at 100 pg
Napthalene-d8 (ISTD)	**4.577**					
Naphthalene	4.599	0.1	1000	0.9996	11.9	102
1-methylnaphthalene	5.195	0.1	1000	0.9996	11.0	104
2-methylnaphthalene	5.349	0.1	1000	0.9996	12.5	103
Biphenyl	5.723	0.1	1000	0.9996	15.1	103
2,6-dimethylnaphthalene	5.750	0.1	1000	0.9999	15.6	102
Acenaphthylene	6.292	0.25	1000	0.9999	1.1 (3.6 at 0.25 pg)	99
Acenaphthene-d10 (ISTD)	**6.382**					
Acenaphthene	6.422	0.1	1000	0.9996	57.3	103
2,3,5-trimethylnaphthalene	6.601	0.1	1000	0.9997	5.0	102
Fluorene	6.933	0.1	1000	0.9995	38.3	104
Dibenzothiophene	8.191	0.1	1000	0.9998	26.9	101
Phenanthrene-d10 (ISTD)	**8.346**					
Phenanthrene	8.388	0.1	1000	0.9997	31.9	103
Anthracene	8.436	0.1	1000	0.9999	6.7	99
1-methylphenanthrene	9.440	0.1	1000	0.9997	7.8	102
Fluoranthene	10.800	0.1	1000	0.9997	30.7	102
Pyrene	11.474	0.1	1000	0.9998	16.1	102
Benzo(a)anthracene	14.657	0.1	1000	0.9997	11.9	101
Chrysene-d12 (ISTD)	**14.809**					
Chrysene	14.892	0.1	1000	0.9999	18.1	99
Benzo(b)fluoranthene	17.738	0.1	1000	0.9997	18.1	102
Benzo(k)fluoranthene	17.803	0.1	1000	0.9999	8.0	101
Benzo(j)fluoranthene	17.886	0.1	1000	0.9961	13.7	98
Benzo(e)pyrene	18.696	0.1	1000	0.9997	26.5	103
Benzo(a)pyrene	18.833	0.1	1000	0.9998	3.2	97
Perylene-d12 (ISTD)	**19.084**					
Perylene	19.156	0.1	1000	0.9999	25.4	98
Dibenz(a,c)anthracene	21.450	0.1	1000	0.9998	3.3	97
Indeno(1,2,3,-cd)pyrene	21.501	0.1	1000	0.9994	7.6	97
Dibenz(a,h)anthracene	21.536	0.1	1000	0.9973	4.5	91
Benzo(g,h,i)perylene	22.258	0.1	1000	0.9999	6.3	99

Selected calibration curves for early- and late-eluting PAHs, including naphthalene, fluorene, indeno(1,2,3,-cd)pyrene, and benzo(g,h,i)perylene are shown in Figure 5. The insets in Figure 5 show the magnified part of the calibration levels of 0.1 to 20 pg to demonstrate excellent accuracy even at low concentrations.

Another challenge to PAH analyses reported in previous literature[5] is ISTD response inconsistency across the calibration range, which can lead to problems with linearity of the method. Under these method conditions, ISTD response was consistent throughout the calibration range with RSDs not exceeding 8%. The RSDs for naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 over a 12-point calibration bracketed with two solvent blanks were 4.8%, 5.7%, 5.8%, 6.1%, and 7.5%, respectively. This was within ±20% typically specified by the regulatory methods with calibration standards.

Use of the Ultra Inert universal low pressure drop liner (4 mm, glass wool) with pulsed splitless injection contributed to the observed method sensitivity, precision, and consistency of the ISTD responses.

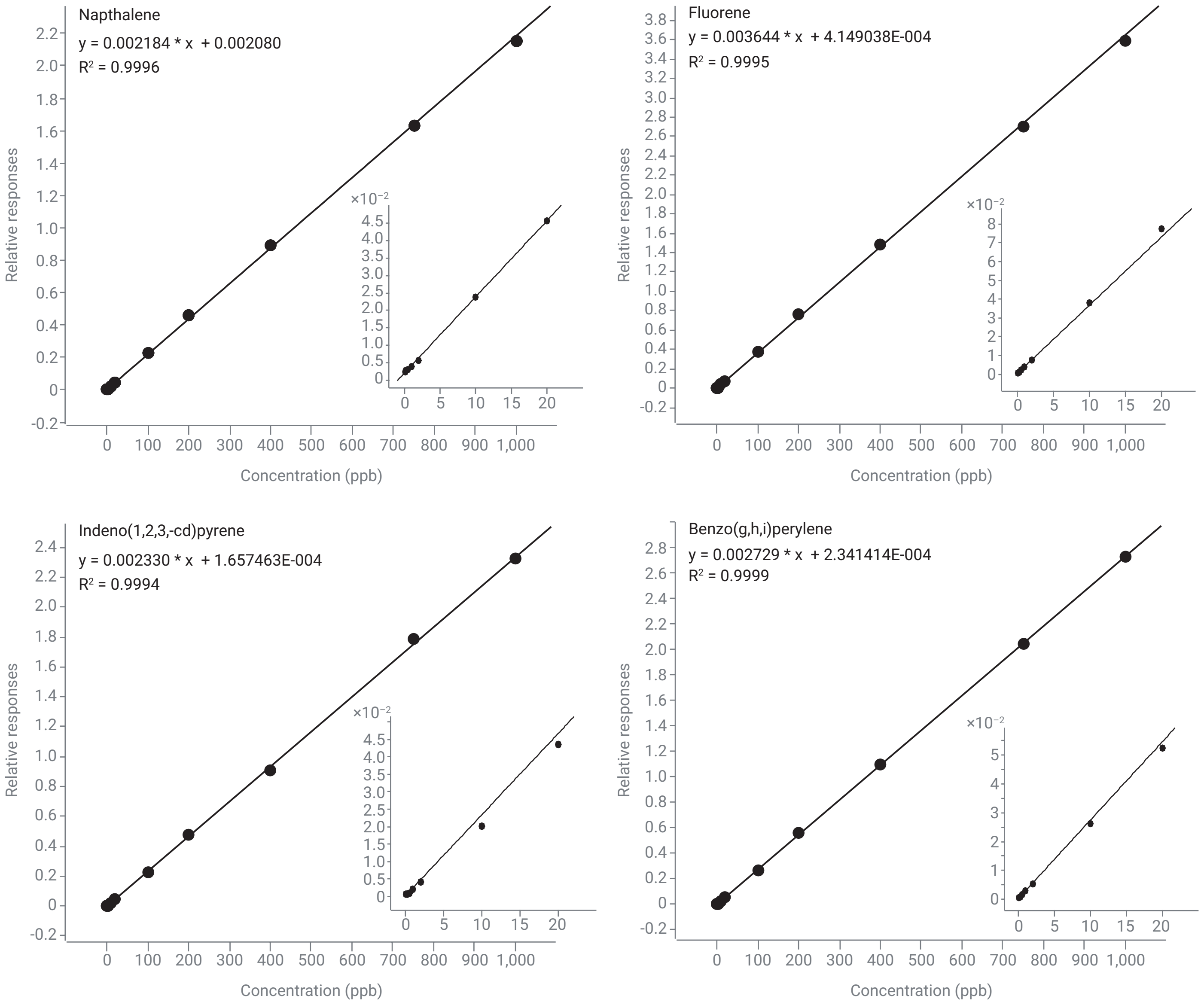


Figure 5. Selected calibration curves over the ranges of 0.1 to 1,000 pg and enlarged 0.1 to 20 pg for early- and late-eluting PAHs, including (a) naphthalene, (b) fluorene, (c) indeno(1,2,3,-cd)pyrene, and (d) benzo(g,h,i)perylene.

Conclusion

The system described here enables successful analysis of PAHs over an extended calibration range of 0.1 to 1,000 pg. The method addresses many of the problems encountered using hydrogen carrier gas and GC/MS PAH analysis. Use of GC/TQ in MRM mode simplifies data review by providing much higher selectivity over spectral interferences from the matrix. Using the 9 mm extractor lens, higher zone temperatures, suitable column dimensions, and the appropriate liner results in substantial improvements in linearity, peak shape, and system robustness. Optimization of the collision energies with hydrogen carrier gas was greatly simplified using the MassHuter Optimizer for GC/TQ.

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Volatile Organic Compounds Analysis in Drinking Water with Headspace GC/MSD Using Hydrogen Carrier Gas and HydroInert Source

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Abstract

An Agilent 8890/5977C GC/MSD system coupled with an Agilent 8697 headspace sampler was successfully used with hydrogen carrier gas for the analysis of volatile organic compounds (VOCs) in drinking water. Recent concerns with the price and availability of helium have led laboratories to look for alternative carrier gases for their GC/MS methods. For GC/MS, hydrogen is the best alternative to helium, and offers potential advantages in terms of chromatographic speed and resolution. However, hydrogen is not an inert gas, and may cause chemical reactions in the mass spectrometer electron ionization (EI) source. This can lead to disturbed ion ratios in the mass spectrum, spectral infidelity, peak tailing, and nonlinear calibration for some analytes. Therefore, a new EI source for GC/MS and GC/MS/MS was developed, and optimized for use with hydrogen carrier gas. The new source, named HydroInert, was used in the system evaluated here. In addition to the new source, the chromatographic conditions were optimized to provide separation of 80 volatile compounds in 7 minutes. Standards and samples were analyzed in both scan and SIM data acquisition modes. For the scan data, spectra were deconvoluted with MassHunter Unknowns Analysis software and searched against NIST 20 to assess the spectral fidelity. In both modes, quantitative calibration was performed for the 80 compounds over the range of 0.05 to 25 µg/L. As demonstrated in this note, the system gives excellent results for the analysis of VOCs in drinking water.

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Introduction

One of the analyses commonly used to ensure that the quality of drinking water is the measurement of volatile organic compounds (VOCs). These compounds can appear in drinking water by contamination from numerous sources, including industrial and commercial operations. Another common source is when VOCs are formed by the addition of chlorine (used to disinfect the water), and react with natural organic matter in the source water. Regulations governing the allowable concentration of VOCs in drinking water vary by country and region, but are typically in the low µg/L (ppb) range. Due to the large number of potential contaminants, and the need to measure them at such low levels, GC/MS systems are commonly used. GC/MS offers both the sensitivity and selectivity required to identify and quantify VOCs. Purge and trap[1] and static headspace[2,3] are two commonly used automated sampling techniques that extract the VOC analytes from water samples and inject them into the GC/MS. This application note describes a system configured to perform static headspace/GC/MS analysis of VOCs in drinking water, optimized for using hydrogen as the carrier gas.

The system configured here was optimized for hydrogen carrier use, employing the following key components and techniques:

- Agilent J&W DB-624 Ultra Inert column: The DB-624 UI column, 20 m × 0.18 mm, 1 µm (part number 121-1324UI) is designed to provide high chromatographic resolution of VOCs when using hydrogen carrier gas. This allowed the separation of 80 VOCs in under 7 minutes.
- The Agilent Inlet Liner, Ultra Inert, splitless, straight 1 mm id (part number 5190-4047) is necessary to connect the transfer line from the headspace unit to the GC column in the inlet. Use of wider inner diameter liners can cause broadening of analyte peaks with low split ratios like that used here.
- Pulsed split injection: Pulsed split injection is helpful in getting the injection bandwidth narrow enough to be compatible with the small diameter column used here. The technique allows a low split ratio, such as 21:1 used in this study, to maintain sensitivity while providing a high split flow during the injection, to rapidly sweep the headspace sample loop. Rapid sweeping of the loop is key to reducing peak broadening, especially for the earliest-eluting compounds.
- Agilent HydroInert source with 9 mm extractor lens: Because hydrogen is used as the carrier gas, the HydroInert source[4] is used. This new EI extractor source was developed and optimized for use with hydrogen carrier gas, and greatly reduces in-source reactions that can cause problems with spectral infidelity, peak tailing, and nonlinear calibration for some analytes like nitrobenzene.
- Spectral deconvolution with Agilent MassHunter Unknowns Analysis software: The Agilent Unknowns Analysis software uses spectral deconvolution to extract clean analyte spectra from those of overlapping peaks. This results in higher library match scores, and greater confidence in peak identifications. NIST20 was used as the reference library.
- Addition of salt: The addition of salts like sodium chloride or sodium sulfate to aqueous headspace samples is commonly used to increase sensitivity of the analysis. The presence of the salt increases the amount of a compound that partitions into the gas phase. Sodium sulfate was chosen for this work.

Both scan and SIM modes of data acquisition were evaluated. Scan is useful for confirming the identity of found targets, and for identifying nontarget compounds. It can also be used retrospectively to search for compounds that may become of interest in the future. SIM has a substantial advantage in the signal-to-noise ratio, and is preferred where quantitation to low levels is required.

Experimental

The Agilent 5977C Inert Plus MSD was coupled to the Agilent 8890 GC equipped with a multimode inlet (MMI) and an Agilent 8697 headspace sampler. A HydroInert source (G7078-60930 for the fully assembled source with 9 mm lens) was used in the MSD, and autotuned using the etune tuning algorithm. The analytical method used an Agilent Ultra Inert straight-through 1.0 mm GC inlet liner (part number 5190-4047) and a DB-624 UI column, 20 m × 0.18 mm, 1 µm (part number 121-1324UI). The 8697 Headspace Sampler was connected to the GC carrier gas inlet line between the GC control pneumatics and the GC injection port. A pulsed split injection was used with the split ratio set to 21:1.

Eight calibration levels ranging from 0.05 to 25 µg/L were prepared in water by spiking 5 µL of a corresponding stock solution (which also included the ISTD) into 10.0 mL of water in a 20 mL headspace vial. Five grams of anhydrous sodium sulfate were weighed into each vial before the addition of water and spiking solution. After capping, each vial was vortexed vigorously for 20 seconds, before placement in the headspace sampler. The spiking stock solutions were prepared in methanol using an Agilent 73-compound standard (DWM-525-1), an Agilent six-compound gas standard (DWM-544-1), and an Agilent three-compound ISTD mix (STM-320N-1), containing fluorobenzene (internal standard), 1,2-dichlorobenzene-d4 (surrogate), and BFB (surrogate). The ISTD/surrogate mix was added to each calibration stock solution at a level to give 5 µg/mL of each compound in the water. Agilent MassHunter Workstation software was used for data acquisition and processing. Figure 1 shows the system configuration used here. The operating parameters are listed in Table 1.

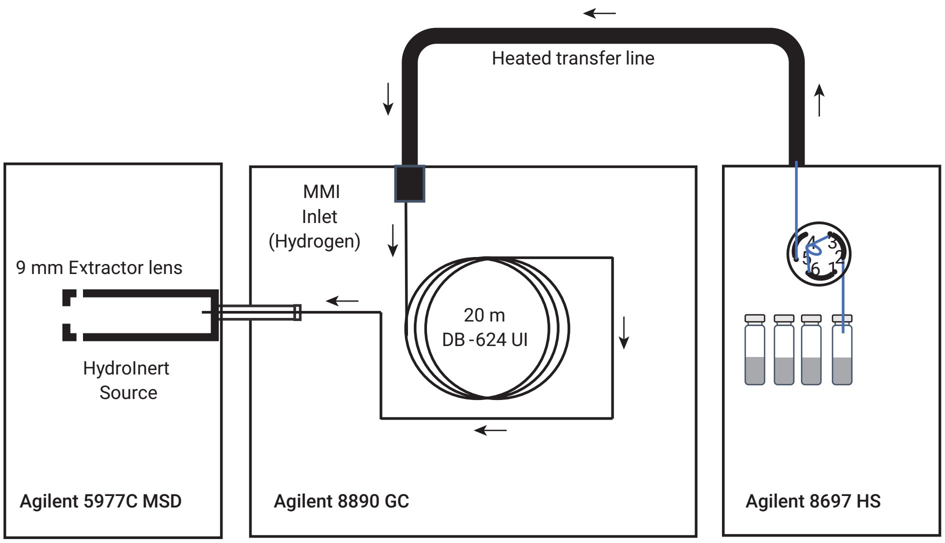


Figure 1. Instrument configuration.

Table 1. Gas chromatograph, mass spectrometer, and headspace sampler parameters for VOCs analysis.

Agilent 8890 GC Parameters	
Parameters	Setpoints
Inlet Temperature	200 °C
Liner	Agilent Ultra Inert inlet liner, splitless, straight, 1 mm id (p/n 5190-4047)
Carrier Gas	Hydrogen
Column Flow	0.95 mL/min constant flow
Injection Mode	Pulsed split
Split Ratio	21:1
Pulse Pressure	26 psig until 0.3 min
Septum Purge Flow	3 mL/min
Column	Agilent DB-624 Ultra Inert, 20 m × 0.18 mm, 1 µm (p/n 121-1324-UI)
Oven Program	35 °C (0.25 min), ramp 25 °C/min to 240 °C (0.2 min) Run time 8.65 min
Agilent 5977C MSD	
MS Source	HydroInert Extractor with 9 mm Extractor Lens
MS Tune	Etune
MSD Transfer Line Temperature	250 °C
MS Source Temperature	250 °C
MS Quad Temperature	200 °C
Scan Range	35 to 260 Da
Scan Speed	A/D samples 4, TID on
EM Gain Factor (Scan mode)	5
SIM Method Dwell Time	10 to 60 ms, varied by time segment to maintain minimum cycle time of 6.7 Hz
EM Gain Factor (SIM Mode)	2

Agilent 8697 Headspace Sampler	
8697 Loop Size	1 mL
Vial Pressurization Gas	Nitrogen
HS Loop Temperature	75 °C
HS Oven Temperature	75 °C
HS Transfer Line Temperature	115 °C
Vial Equilibration	12.00 min
Injection Duration	0.30 min
GC Cycle Time	15.00 min
Vial Size	20 mL
Vial Shaking	Level 9, 250 shakes/min with acceleration of 980 cm/s²
Fill Mode	Default
Fill Flow	50
Fill Pressure	10 psi
Pressure Equilibration Time	0.1 min
Postinjection Purge	100 mL/min for 2 min

Results and discussion

Scan results

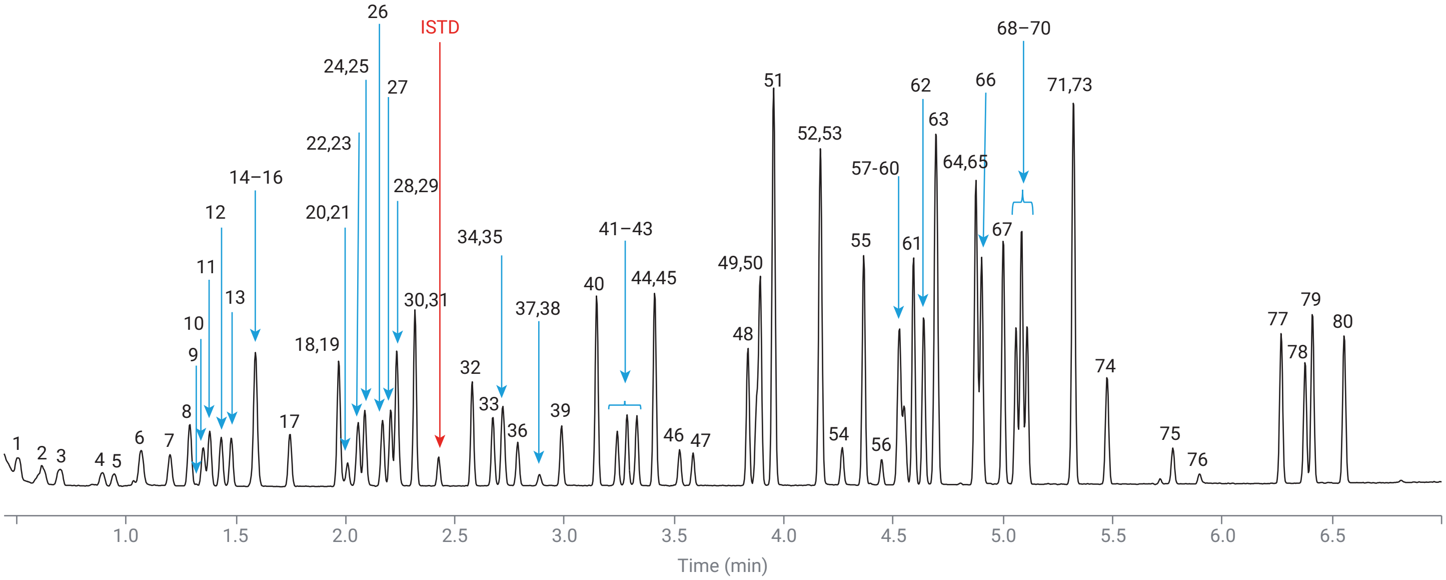


Figure 2. Total ion chromatogram (TIC) from the scan analysis of the 25 µg/L standard. The numbers identifying the peaks correspond to the first column in Table 2.

Table 2. Peak identifications, calibration results, and deconvoluted library match scores against NIST20 for the scan analysis.

Peak No.	Compound	RT (min)	Tgt *m/z*	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R^2	CF	CF Weight	Rel. Std. Error	LMS NIST20	
	Fluorobenzene [ISTD]	2.425	96	77								97	
1	Dichlorodifluoromethane	0.508	85	87	12.5	0.1	25	0.9989	Linear	1/x	17.3	92	
2	Chloromethane	0.615	50	52	14.4	0.25	25	0.9977	Linear	1/x	16.2	97	
3	Chloroethene	0.698	62	64	18.4	0.05	25	0.9995	Linear	1/x	9	91	
4	Bromomethane	0.891	94	96	21.7	1	25	0.9995	Linear	1/x	4.2	96	
5	Ethyl Chloride	0.945	64	66	13.6	0.25	25	0.9995	Linear	1/x	6.5	92	
6	Trichloromonofluoromethane	1.067	101	103	9.6	0.05	25	0.9994	Linear	1/x	9.6	96	
7	Ethyl ether	1.198	74	59	12.8	0.25	25	0.9992	Linear	1/x	11.4	97	
8	1,1-Dichloroethene	1.288	61	96	6.7	0.05	25	0.9993	Linear	1/x	7.3	98	
9	Acetone	1.317	58	43	112.5	1	25	0.9770	Linear	1/x	22.9	87	*
10	Iodomethane	1.350	142	127	14.6	0.05	25	0.9997	Linear	1/x	7.4	99	
11	Carbon disulfide	1.379	76		16.4	0.05	25	0.9997	Linear	1/x	5.7	95	
12	Allyl chloride	1.432	76	41	13.9	0.1	25	0.9982	Linear	1/x	17.2	97	
13	Methylene chloride	1.478	84	49	5.0	0.1	25	0.9996	Linear	1/x	5.1	97	
14	Acrylonitrile	1.572	52	53	16.1	0.5	25	0.9940	Linear	1/x	16.3	90	
15	*trans*-1,2-Dichloroethylene	1.586	61	96	15.9	0.05	25	0.9991	Linear	1/x	17.5	99	
16	Methyl tert-butyl ether	1.592	73	57	8.3	0.05	25	0.9991	Linear	1/x	9.6	98	
17	1,1-Dichloroethane	1.745	63	65	9.4	0.05	25	0.9998	Linear	1/x	5.2	97	
18	*cis*-1,2-Dichloroethylene	1.966	61	96	7.9	0.05	25	0.9998	Linear	1/x	6.1	95	
19	2,2-Dichloropropane	1.969	77	79	3.1	0.5	25	0.9994	Linear	1/x	3.7	80	**
20	Propanenitrile	1.993	54	52	14.5	0.5	25	0.9943	Linear	1/x	16.4	67	*
21	2-Propenoic acid, methyl ester	2.008	55	85	12.2	0.1	25	0.9991	Linear	1/x	8.5	97	

Peak No.	Compound	RT (min)	Tgt *m/z*	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R^2	CF	CF Weight	Rel. Std. Error	LMS NIST20	
22	Methylacrylonitrile	2.052	67	52	4.6	0.5	25	0.9994	Linear	1/x	4.4	95	
23	Bromochloromethane	2.059	130	128	15.4	0.1	25	0.9946	Linear	1/x	14.2	97	
24	Trichloromethane	2.086	83	85	7.0	0.1	25	0.9989	Linear	1/x	11.5	98	
25	Tetrahydrofuran	2.090	72	71	19.1	0.25	25	0.9959	Linear	1/x	10.3	96	
26	1,1,1-Trichloroethane	2.168	97	99	14.9	0.05	25	0.9995	Linear	1/x	9.6	98	
27	1-Chlorobutane	2.205	56	41	5.1	0.1	25	0.9997	Linear	1/x	6.6	97	
28	1,1-Dichloropropene	2.231	75	110	18.5	0.05	25	0.9980	Linear	1/x	13.8	96	
29	Carbon Tetrachloride	2.235	117	119	8.7	0.1	25	0.9983	Linear	1/x	9.4	96	
30	Benzene	2.315	78	77	10.4	0.05	25	0.9991	Linear	1/x	11.4	94	
31	1,2-Dichloroethane	2.316	62	64	15.5	0.05	25	0.9989	Linear	1/x	9.8	98	
32	Trichloroethylene	2.577	130	132	18.7	0.1	25	0.9981	Linear	1/x	12.4	99	
33	1,2-Dichloropropane	2.671	63	62	10.8	0.1	25	0.9997	Linear	1/x	9	98	
34	Methyl methacrylate	2.713	100	69	8.4	0.1	25	0.9991	Linear	1/x	10.5	98	
35	Dibromomethane	2.722	174	172	13.6	0.1	25	0.9989	Linear	1/x	18	98	
36	Bromodichloromethane	2.785	83	85	14.5	0.1	25	0.9997	Linear	1/x	4.1	98	
37	2-Nitropropane	2.883	43	41	19.4	0.5	25	0.9973	Linear	1/x	16.2	93	
38	Chloromethyl cyanide	2.887	75	77	51.4	1	25	0.9947	Linear	1/x	9.7	63	*
39	*cis*-1,3-Dichloropropene	2.985	75	110	12.9	0.1	25	0.9956	Linear	1/x	12.4	98	
40	Toluene	3.145	91	92	2.9	0.05	25	0.9995	Linear	1/x	4.3	99	
41	*trans*-1,3-Dichloropropene	3.239	75	110	7.1	0.05	25	0.9963	Linear	1/x	9.3	98	
42	Ethyl methacrylate	3.283	69	41	9.6	0.05	25	0.9989	Linear	1/x	10.5	98	
43	1,1,2-Trichloroethane	3.328	97	99	11.0	0.1	25	0.9994	Linear	1/x	7.8	98	
44	Tetrachloroethylene	3.410	164	166	10.0	0.1	25	0.9991	Linear	1/x	11.3	91	
45	1,3-Dichloropropane	3.412	76	78	17.9	0.05	25	0.9978	Linear	1/x	10.7	90	
46	Dibromochloromethane	3.524	129	127	6.0	0.1	25	0.9998	Linear	1/x	5.2	98	
47	1,2-Dibromoethane	3.585	109	107	6.9	0.25	25	0.9989	Linear	1/x	9.1	99	
48	Chlorobenzene	3.835	112	114	8.7	0.05	25	0.9951	Linear	1/x	12.8	99	
49	1,1,1,2-Tetrachloroethane	3.875	133	131	10.4	0.1	25	0.9968	Linear	1/x	14.4	96	
50	Ethylbenzene	3.892	91	106	5.6	0.05	25	0.9992	Linear	1/x	4.3	98	
51	*m*-Xylene	3.953	91	106	7.7	0.05	25	0.9991	Linear	1/x	4.6	99	
52	*o*-Xylene	4.164	91	106	6.7	0.05	25	0.9995	Linear	1/x	10.8	89	
53	Styrene	4.169	104	103	13.0	0.05	25	0.9972	Linear	1/x	8.8	96	
54	Tribromomethane	4.266	173	171	14.1	0.1	25	0.9993	Linear	1/x	11.2	99	
55	Isopropylbenzene	4.364	105	120	15.9	0.05	25	0.9978	Linear	1/x	6.9	98	
56	*p*-Bromofluorobenzene [SURR]	4.446	174	176								97	
57	1,1,2,2-Tetrachloroethane	4.521	83	85	9.4	0.1	25	0.9981	Linear	1/x	12.4	97	
58	Bromobenzene	4.530	158	156	11.4	0.1	25	0.9963	Linear	1/x	15.9	97	
59	1,2,3-Trichloropropane	4.548	110	112	8.5	0.25	25	0.9960	Linear	1/x	14.7	84	
60	*trans*-1,4-Dichloro-2-butene	4.555	89	88	9.9	0.25	25	0.9985	Linear	1/x	10.7	65	**
61	Propylbenzene	4.592	91	120	8.6	0.05	25	0.9989	Linear	1/x	8.1	98	
62	2-Chlorotoluene	4.638	91	126	7.9	0.05	25	0.9993	Linear	1/x	7.3	98	
63	Mesitylene	4.692	105	120	11.6	0.05	25	0.9972	Linear	1/x	8	91	
64	*tert*-Butylbenzene	4.876	134	91	17.4	0.25	25	0.9954	Linear	1/x	15.5	97	
65	Pentachloroethane	4.881	167	165	13.3	0.1	25	0.9967	Linear	1/x	17.2	86	
66	1,2,4-Trimethylbenzene	4.903	105	120	11.8	0.05	25	0.9975	Linear	1/x	8.4	98	
67	1-Methylpropyl benzene	5.001	105	134	19.0	0.05	25	0.9955	Linear	1/x	11.9	98	

Peak No.	Compound	RT (min)	Tgt *m/z*	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R^2	CF	CF Weight	Rel. Std. Error	LMS NIST20	
68	1,3-Dichlorobenzene	5.060	146	148	10.8	0.05	25	0.9979	Linear	1/x	13.3	99	
69	*p*-Cymene (4-Isopropyltoluene)	5.086	119	134	9.9	0.05	25	0.9994	Linear	1/x	6.9	97	
70	1,4-Dichlorobenzene	5.110	146	148	9.7	0.05	25	0.9979	Linear	1/x	17.2	99	
71	1,2-Dichlorobenzene-D4 [SURR]	5.313	152	150								78	**
72	*n*-Butylbenzene	5.322	91	92	9.5	0.1	25	0.9956	Linear	1/x	12.9	96	
73	1,2-Dichlorobenzene	5.325	146	148	12.0	0.05	25	0.9993	Quadratic	1/x	12.6	92	
74	Hexachloroethane	5.476	166	164	13.7	0.1	25	0.9979	Linear	1/x	14.4	97	
75	1,2-Dibromo-3-chloropropane	5.775	155	75	5.1	0.25	25	0.9982	Linear	1/x	8.2	98	
76	Nitrobenzene	5.896	77	51	15.6	1	25	0.9981	Linear	1/x	5.5	94	
77	1,2,4-Trichlorobenzene	6.270	180	182	13.5	0.05	10	0.9990	Linear	1/x	15.1	99	
78	1,1,2,3,4,4-Hexachlorobuta-1,3-diene	6.380	225	223	8.6	0.05	25	0.9997	Linear	1/x	9.6	91	
79	Naphthalene	6.413	128	127	7.1	0.05	25	0.9986	Linear	1/x	11.4	99	
80	1,2,3-Trichlorobenzene	6.558	180	182	13.4	0.05	25	0.9942	Linear	1/x	12.5	99	

* Library match score lower due to low response of compound.

** Library match score lower due to overlapping spectra not completely removed by deconvolution.

Initial calibration (ICAL) with scan data

The chromatographic parameters used in the method resulted in good separation of the 80 VOC compounds in less than 7 minutes, as shown in Figure 2. While there are overlapping peaks, their response was measured selectively with the quantifier ions chosen. Most compounds had sufficient response to be measured at or below 0.1 µg/L, and exhibit very good linearity. The average calibration range was 0.16 to 25 µg/L with an average R^2 of 0.9978. If necessary, the relative standard error (RSE) value was used to guide removal of the lowest, and in one case highest, calibration points, to achieve an RSE value of <20% (except for acetone). The average Response Factor RSD was <20 for 76 analytes. As expected, polar compounds with higher solubility in water were the worst performers. Acetone is an example, where it also had a contamination issue as observed in the blank, resulting in poor calibration results. A typical example is shown in Figure 3, with the lowest calibrator and calibration curve for iodomethane.

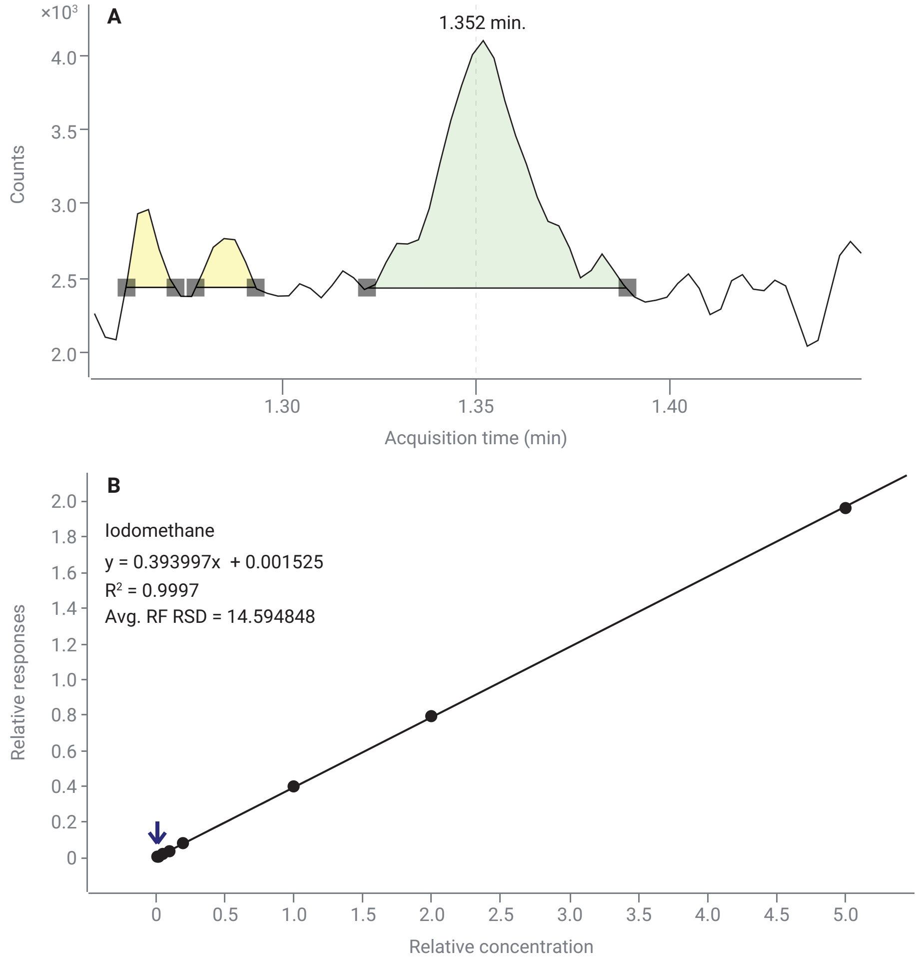


Figure 3. (A) quantifier EIC for iodomethane 0.05 µg/L calibration standard. (B) calibration curve for iodomethane from 0.05 µg/L to 25 µg/L.

Spectral fidelity

The 25 µg/L VOC standard was analyzed with the MassHunter Unknowns Analysis software, where spectra of the compounds were deconvoluted and searched against the NIST20 library. As seen in Table 2, the library match scores (LMS) are excellent, with an average of 94. There were only six compounds with LMS scores below 90, and these were due to low response and/or interference from overlapping peaks not completely removed by deconvolution. Nitrobenzene (compound 76 in Table 2) gave a very good LMS value of 94. Nitrobenzene reacts readily with hydrogen in a conventional MS source to produce aniline[4], resulting in low LMS values typically in the 60s. The HydroInert source greatly reduces in-source reactions with hydrogen, resulting in the high LMS value for nitrobenzene.

Initial calibration with SIM data

The results of the SIM mode calibration are listed in Table 3. As expected, for most compounds, SIM provided excellent calibration linearity and measurement at or below 0.05 µg/L. The average calibration range was 0.07 to 24 µg/L, with an average R^2 of 0.9990. If necessary, the relative standard error (RSE) value was used to guide removal of the lowest and highest calibration points, to achieve an RSE value of <20%, and for choosing between a linear or quadratic fit. For some compounds, a linear fit would meet the <20% RSE criteria, but come close to the limit. However, use of a quadratic fit would significantly improve the RSE. For example, *tert*-butylbenzene had an RSE of 18.3 with a linear fit, but changing to quadratic lowered the RSE to 8.1. Similar improvements were seen with some of the other substituted benzenes as well. As observed with the scan data calibration, the average response factor RSD was <20 for 76 analytes.

SIM results

Table 3. Calibration results, and method detection limits (MDL) using SIM acquisition.

Peak No.	Compound Name	RT (min)	Tgt *m/z*	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R^2	CF	CF Weight	Rel. Std. Error	Conc. for MDL	MDL (µg/L)
	Fluorobenzene [ISTD]	2.425	96	77									
1	Dichlorodifluoromethane	0.508	85	87	15.3	0.05	25	0.9994	Linear	1/x	11.6	0.10	0.011
2	Chloromethane	0.615	50	52	7.3	0.1	25	0.9997	Linear	1/x	8.4	0.10	0.022
3	Chloroethene	0.698	62	64	4.1	0.05	25	0.9998	Linear	1/x	4.7	0.05	0.008
4	Bromomethane	0.891	94	96	4.1	0.05	25	0.9999	Linear	1/x	4.4	0.10	0.029
5	Ethyl Chloride	0.945	64	66	4.5	0.05	25	0.9998	Linear	1/x	4.7	0.05	0.010
6	Trichloromonofluoromethane	1.067	101	103	4.1	0.05	25	0.9997	Linear	1/x	4.3	0.05	0.008
7	Ethyl ether	1.198	74	59	6.4	0.05	25	0.9994	Linear	1/x	11	0.05	0.017
8	1,1-Dichloroethene	1.288	61	96	5.9	0.05	25	0.9996	Linear	1/x	5.3	0.05	0.006
9	Acetone	1.317	58	43	102.2	1	10	0.9994	Linear	1/x	3.5	[cont]	
10	Iodomethane	1.350	142	127	3.3	0.05	25	0.9992	Linear	1/x	4.8	0.05	0.006
11	Carbon disulfide	1.379	76		12.6	0.1	25	0.9994	Linear	1/x	4.6	0.05	0.003
12	Allyl chloride	1.432	76	41	4.9	0.05	25	0.9997	Linear	1/x	6.4	0.05	0.014
13	Methylene chloride	1.478	84	49	12.2	0.1	25	0.9999	Linear	1/x	5.2	0.05	0.007
14	Acrylonitrile	1.572	52	53	8.3	0.1	25	0.9999	Linear	1/x	5.4	[0.25]	
15	*trans*-1,2-Dichloroethylene	1.586	61	96	7.1	0.05	25	0.9997	Linear	1/x	5	0.05	0.007
16	Methyl tert-butyl ether	1.592	73	57	4.2	0.05	25	0.9995	Linear	1/x	7.5	0.05	0.003
17	1,1-Dichloroethane	1.745	63	65	3.7	0.05	25	0.9998	Linear	1/x	4.6	0.05	0.003
18	*cis*-1,2-Dichloroethylene	1.966	61	96	10.1	0.05	25	0.9996	Linear	1/x	7.3	0.05	0.007
19	2,2-Dichloropropane	1.969	77	79	3.6	0.05	25	0.9999	Linear	1/x	4.2	0.10	0.017
20	Propanenitrile	1.993	54	52	5.0	0.25	25	0.9996	Linear	1/x	4.3	[0.25]	
21	2-Propenoic acid, methyl ester	2.008	55	85	11.0	0.05	25	0.9996	Linear	1/x	14.8	0.10	0.029
22	Methylacrylonitrile	2.052	67	52	7.0	0.05	25	0.9988	Linear	1/x	11.4	0.10	0.032
23	Bromochloromethane	2.059	130	128	4.2	0.25	25	0.9991	Linear	1/x	3.5	0.10	0.019
24	Trichloromethane	2.086	83	85	12.2	0.25	10	0.9997	Linear	1/x	1.8	0.05	0.011
25	Tetrahydrofuran	2.090	72	71	3.3	0.05	25	0.9999	Linear	1/x	4.2	0.05	0.030

Peak No.	Compound Name	RT (min)	Tgt MZ	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R^2	CF	CF Weight	Rel. Std. Error	Conc. for MDL	MDL (µg/L)
26	1,1,1-Trichloroethane	2.168	97	99	4.9	0.05	25	0.9995	Linear	1/x	5.5	0.05	0.007
27	1-Chlorobutane	2.205	56	41	11.7	0.05	25	0.9997	Linear	1/x	7.3	0.05	0.007
28	1,1-Dichloropropene	2.231	75	110	7.3	0.05	25	0.9960	Linear	1/x	16.7	0.05	0.007
29	Carbon Tetrachloride	2.235	117	119	7.5	0.05	25	0.9974	Linear	1/x	13.1	0.05	0.015
30	Benzene	2.315	78	77	4.0	0.05	25	0.9998	Linear	1/x	3.5	0.05	0.004
31	1,2-Dichloroethane	2.316	62	64	3.0	0.05	25	0.9993	Linear	1/x	3.3	0.05	0.005
32	Trichloroethylene	2.577	130	132	5.6	0.05	25	0.9993	Linear	1/x	6.9	0.05	0.006
33	1,2-Dichloropropane	2.671	63	62	4.9	0.05	25	0.9998	Linear	1/x	4.6	0.05	0.011
34	Methyl methacrylate	2.713	100	69	9.4	0.05	25	0.9994	Linear	1/x	10.6	0.05	0.033
35	Dibromomethane	2.722	174	172	5.7	0.05	25	0.9996	Linear	1/x	6.3	0.05	0.009
36	Bromodichloromethane	2.785	83	85	3.0	0.05	25	0.9999	Linear	1/x	3.8	0.05	0.011
37	2-Nitropropane	2.883	43	41	8.9	0.1	25	0.9998	Linear	1/x	8.6	0.10	0.041
38	Chloromethyl cyanide	2.887	75	77	81.1	0.25	25	0.9997	Quadratic	1/x	7.6	[0.25]	
39	*cis*-1,3-Dichloropropene	2.985	75	110	3.8	0.05	10	0.9994	Linear	1/x	3.6	0.05	0.003
40	Toluene	3.145	91	92	5.2	0.05	25	0.9997	Linear	1/x	4	0.05	0.003
41	*trans*-1,3-Dichloropropene	3.239	75	110	6.3	0.05	25	0.9956	Linear	1/x	12	0.05	0.005
42	Ethyl methacrylate	3.283	69	41	4.6	0.05	25	0.9990	Linear	1/x	4.7	0.05	0.008
43	1,1,2-Trichloroethane	3.328	97	99	5.4	0.05	25	0.9998	Linear	1/x	2.5	0.05	0.034
44	Tetrachloroethylene	3.410	164	166	5.9	0.05	25	0.9994	Linear	1/x	9.9	0.05	0.005
45	1,3-Dichloropropane	3.412	76	78	5.8	0.05	25	0.9988	Linear	1/x	5.7	0.05	0.007
46	Dibromochloromethane	3.524	129	127	4.2	0.05	25	0.9999	Linear	1/x	4.6	0.05	0.008
47	1,2-Dibromoethane	3.585	109	107	8.1	0.05	25	0.9993	Linear	1/x	3.6	0.05	0.005
48	Chlorobenzene	3.835	112	114	6.6	0.05	25	0.9948	Linear	1/x	12.9	0.05	0.002
49	1,1,1,2-Tetrachloroethane	3.875	133	131	5.0	0.05	25	0.9991	Linear	1/x	9.1	0.05	0.007
50	Ethylbenzene	3.892	91	106	5.0	0.05	25	0.9994	Linear	1/x	4.7	0.05	0.005
51	*m*-Xylene	3.953	91	106	4.6	0.05	25	0.9996	Linear	1/x	4.2	0.05	0.001
52	*o*-Xylene	4.164	91	106	6.5	0.05	25	0.9999	Linear	1/x	4.9	0.05	0.004
53	Styrene	4.169	104	103	7.1	0.05	25	0.9988	Linear	1/x	6	0.05	0.005
54	Tribromomethane	4.266	173	171	5.4	0.05	25	0.9999	Linear	1/x	4.7	0.05	0.003
55	Isopropylbenzene	4.364	105	120	6.0	0.05	25	0.9981	Linear	1/x	6.2	0.05	0.004
56	*p*-Bromofluorobenzene [SURR]	4.446	174	176									
57	1,1,2,2-Tetrachloroethane	4.521	83	85	8.0	0.05	25	0.9999	Quadratic	1/x	4.8	0.05	0.006
58	Bromobenzene	4.530	158	156	7.1	0.05	25	0.9998	Linear	1/x	5.4	0.05	0.003
59	1,2,3-Trichloropropane	4.548	110	112	8.2	0.05	25	0.9970	Linear	1/x	12.2	0.05	0.024
60	*trans*-1,4-Dichloro-2-butene	4.555	89	88	13.0	0.25	25	0.9999	Linear	1/x	2.2	[0.25]	
61	Propylbenzene	4.592	91	120	5.4	0.05	25	0.9988	Linear	1/x	5.8	0.05	0.008
62	2-Chlorotoluene	4.638	91	126	4.1	0.05	25	0.9996	Linear	1/x	4.7	0.05	0.006
63	Mesitylene	4.692	105	120	5.9	0.05	25	0.9969	Linear	1/x	8.6	0.05	0.008
64	*tert*-Butylbenzene	4.876	134	91	10.5	0.05	25	0.9997	Quadratic	1/x	8.1	0.05	0.004
65	pentachloroethane	4.881	167	165	6.6	0.05	25	0.9953	Linear	1/x	6.6	0.05	0.009
66	1,2,4-Trimethylbenzene	4.903	105	120	6.8	0.05	25	0.9985	Linear	1/x	5.3	0.05	0.007
67	1-Methylpropyl benzene	5.001	105	134	5.3	0.05	10	0.9995	Linear	1/x	5.1	0.05	0.004
68	1,3-Dichlorobenzene	5.060	146	148	5.0	0.05	25	0.9990	Linear	1/x	7.6	0.05	0.003
69	*p*-Cymene (4-Isopropyltoluene)	5.086	119	134	5.1	0.05	25	0.9994	Linear	1/x	8.2	0.05	0.009
70	1,4-Dichlorobenzene	5.110	146	148	5.4	0.05	25	0.9985	Linear	1/x	8.5	0.05	0.004
71	1,2-Dichlorobenzene-D4 [SURR]	5.313	152	150									
72	*n*-Butylbenzene	5.322	91	92	9.8	0.05	25	0.9997	Quadratic	1/x	6.3	0.05	0.012

Peak No.	Compound Name	RT (min)	Tgt MZ	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R^2	CF	CF Weight	Rel. Std. Error	Conc. for MDL	MDL (µg/L)
73	1,2-Dichlorobenzene	5.325	146	148	5.4	0.05	10	0.9995	Linear	1/x	6.3	0.05	0.003
74	Hexachloroethane	5.476	166	164	5.0	0.05	25	0.9996	Linear	1/x	8.2	0.05	0.008
75	1,2-Dibromo-3-chloropropane	5.775	155	75	15.2	0.05	25	0.9991	Linear	1/x	7.9	0.05	0.017
76	Nitrobenzene	5.896	77	51	8.5	0.25	25	0.9992	Linear	1/x	9.3	[0.25]	
77	1,2,4-Trichlorobenzene	6.270	180	182	6.1	0.05	10	0.9996	Linear	1/x	5.5	0.05	0.007
78	1,1,2,3,4,4-Hexachlorobuta-1,3-diene	6.380	225	223	13.3	0.05	25	0.9996	Linear	1/x	5.9	0.05	0.006
79	Naphthalene	6.413	128	127	7.9	0.05	25	0.9989	Linear	1/x	8.9	0.05	0.003
80	1,2,3-Trichlorobenzene	6.558	180	182	4.0	0.05	10	0.9996	Linear	1/x	4.9	0.05	0.006

Figure 4 shows a typical example with the lowest calibrator and calibration curve for iodomethane. The improved signal-to-noise ratio provided by SIM, relative to that shown in Figure 3, is clear.

Method detection limits

An MDL study was performed after completion of the initial calibration. Eight trials were performed at the lowest level of calibration, 0.05 µg/L. The calculated MDLs were obtained by applying the formula shown in Equation 1. For compounds with higher reporting limits, eight trials were performed at the concentration of 0.1 µg/L. Table 3 lists the calculated MDLs for 80 VOCs. Six compounds had insufficient response, even at the 0.1 µg/L level, so the lowest calibration level used is listed instead in bold and square brackets. As noted in the scan results, acetone also had a contamination issue as observed in the blank, resulting in poor calibration results. The average MDL for the 80 compounds was 0.026 µg/L.

Equation 1. Formula for MDL calculations.

MDL = s · t(n – 1, 1 – alpha = 99)
= s · 2.998

Where:

t(n – 1, 1 – alpha) = t value for the 99% confidence level with n – 1 degrees of freedom

n = number of trials (8)

s = standard deviation of the eight trials

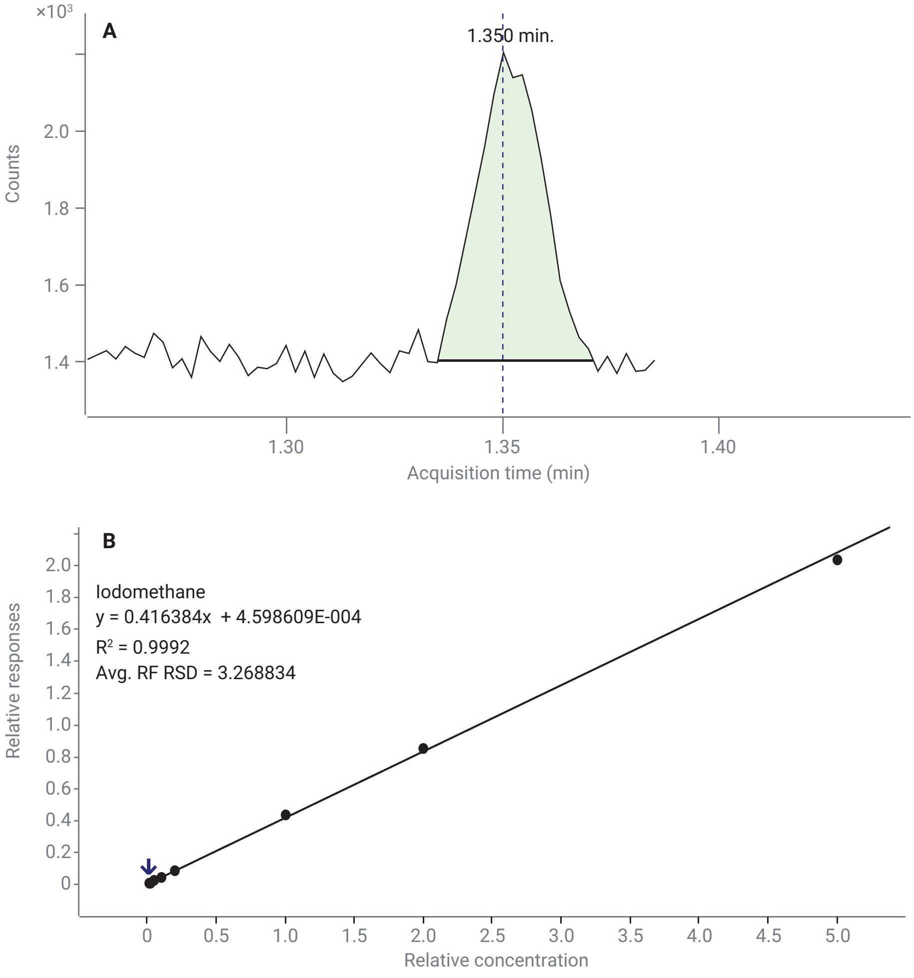


Figure 4. SIM results for iodomethane. (A) quantifier EIC for iodomethane 0.05 µg/L calibration standard. (B) calibration curve for iodomethane from 0.05 µg/L to 25 µg/L.

VOCs found in drinking water

Samples of municipal tap water from sources in the state of Pennsylvania were analyzed using both the scan and SIM methods. Several VOCs were identified with MassHunter Unknowns Analysis and by searching the deconvoluted spectra against the NIST20 library. The chromatograms from two of the samples are shown in Figure 5. The concentration of VOCs was determined using MassHunter Quantitative Analysis, with both the scan and SIM calibrations. The results are presented in Table 4.

Trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane (collectively known as the trihalomethanes) are very common in municipal water treated with chlorine for disinfection purposes. They are the products of reaction between chlorine and naturally occurring humic and fulvic acids, often present in source water. All trihalomethanes were confirmed in both samples with precisely matching retention times, qualifier ion ratios, and, except for tribromomethane, with good LMS search results. As expected, LMS values decrease with decreasing concentration of the analyte. The *cis*-1,2-dichloroethylene and tetrachloroethylene are commonly found at trace levels in ground water from areas with a history of industrial activity. Methyl *tert*-butyl ether (MTBE) was an additive to gasoline several years ago, used in response to federal mandates requiring specified levels of organic oxygen in gasoline. Its use was later banned when it began showing up in ground water as the result of leaking underground storage tanks at gasoline stations.

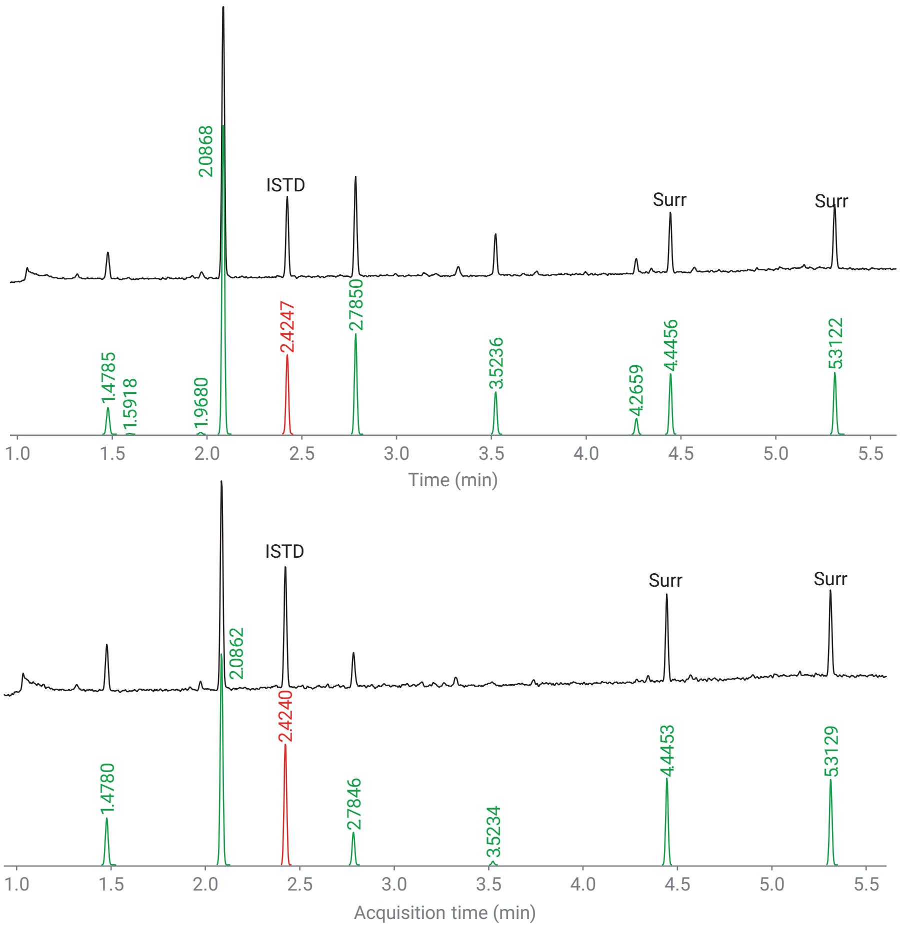


Figure 5. TIC (black) and deconvolution component (green) chromatograms of tap water samples. ISTD is shown in red. Top: Sample from Eastern Pennsylvania. Bottom: Sample from Southeastern Pennsylvania.

Table 4. Results from analysis of tap water samples.

Name	RT (min)	Eastern PA			Southeastern PA		
		Scan	Scan	SIM	Scan	Scan	SIM
		LMS NIST20	Conc. (µg/L)	Conc. (µg/L)	LMS NIST20	Conc. (µg/L)	Conc. (µg/L)
Methyl *tert*-butyl ether	1.592	56	0.08	0.08			
cis-1,2-Dichloroethylene	1.968	71	0.19	0.20			
Trichloromethane	2.087	98	43.47	44.08	97	21.03	20.90
Bromodichloromethane	2.785	98	21.81	22.07	92	4.82	4.85
Tetrachloroethylene	3.410			0.05			
Dibromochloromethane	3.524	98	11.34	10.80	68	0.69	0.69
Tribromomethane	4.266	97	3.97	3.71			0.02

Figure 6 shows the benefits of using both the scan and SIM methods on tap water samples. Spectral matching provides added confidence in the identification of compounds in the water samples. The scan data were processed in Agilent MassHunter Quantitative Unknowns Analysis software, which provides streamlined automated deconvolution and library searching. Previous approaches to processing scan data for library searching rely on comparing a baseline-subtracted apex spectrum of a peak to reference spectra. That approach can work well with a limited number of peaks, to identify when there are no chromatographic interferences with the peak. However, samples containing significant levels of overlapping chromatographic peaks can interfere with the process, making analyte identification challenging. The automated deconvolution and library searching in MassHunter Unknowns Analysis greatly simplifies the processing of spectral data.

Figure 6 shows the extracted SIM quantifier ions and deconvoluted spectra for four of the seven VOCs found in the Eastern PA water sample. Dibromochloromethane [A] is confidently identified with an RT that precisely matches that in the calibration table, an acceptable ratio of the qualifier to quantifier responses (not shown), and a very high library match score.

As the concentration of an analyte decreases, the signal-to-noise ratio in the both the spectra and quantifier chromatograms also decrease. In Figure 6, the spectral information is useful down to about 0.1 µg/L. The SIM data, which identifies using precise RT matching and the ratio of the qualifier to quantifier response can be used to lower levels.

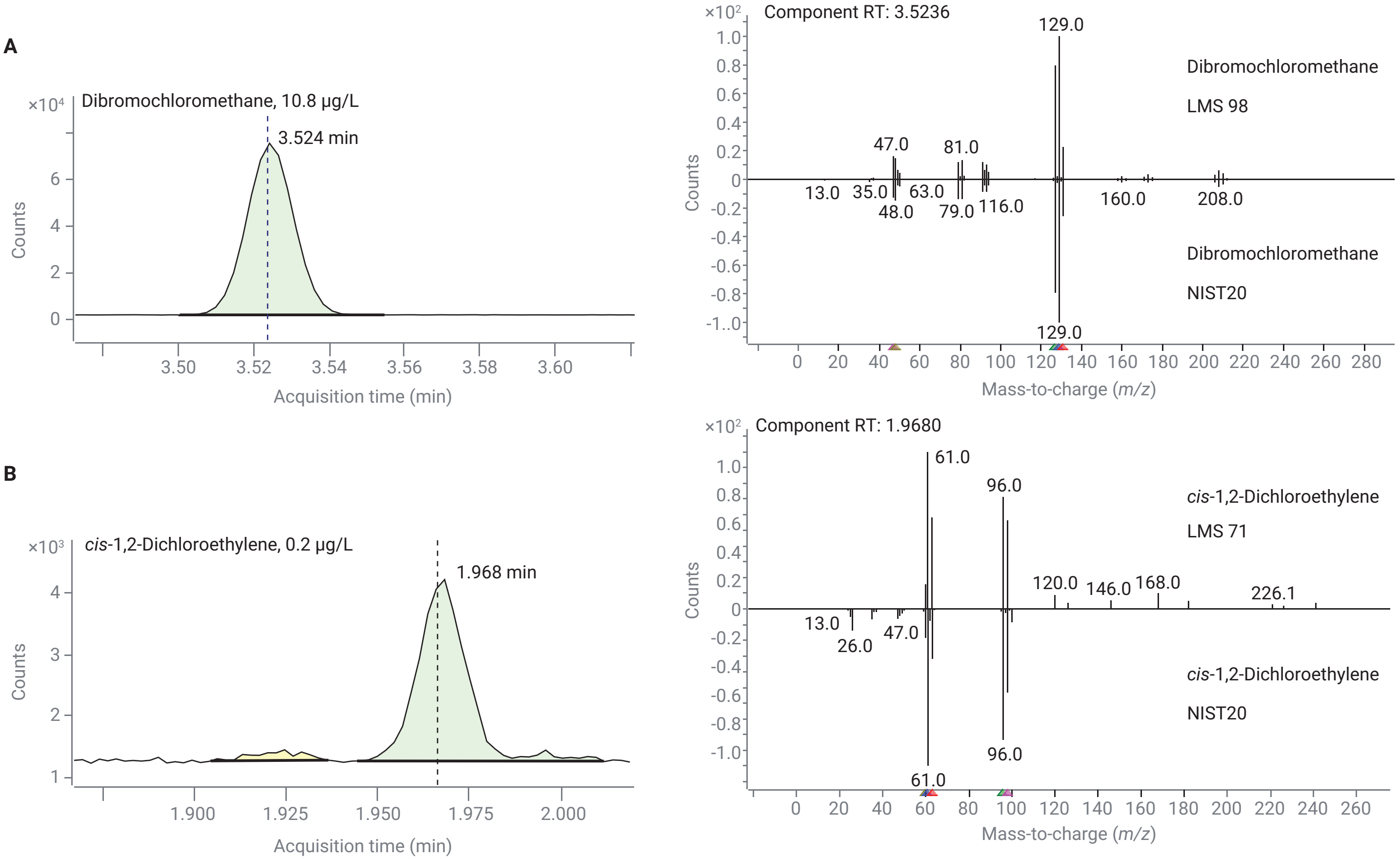
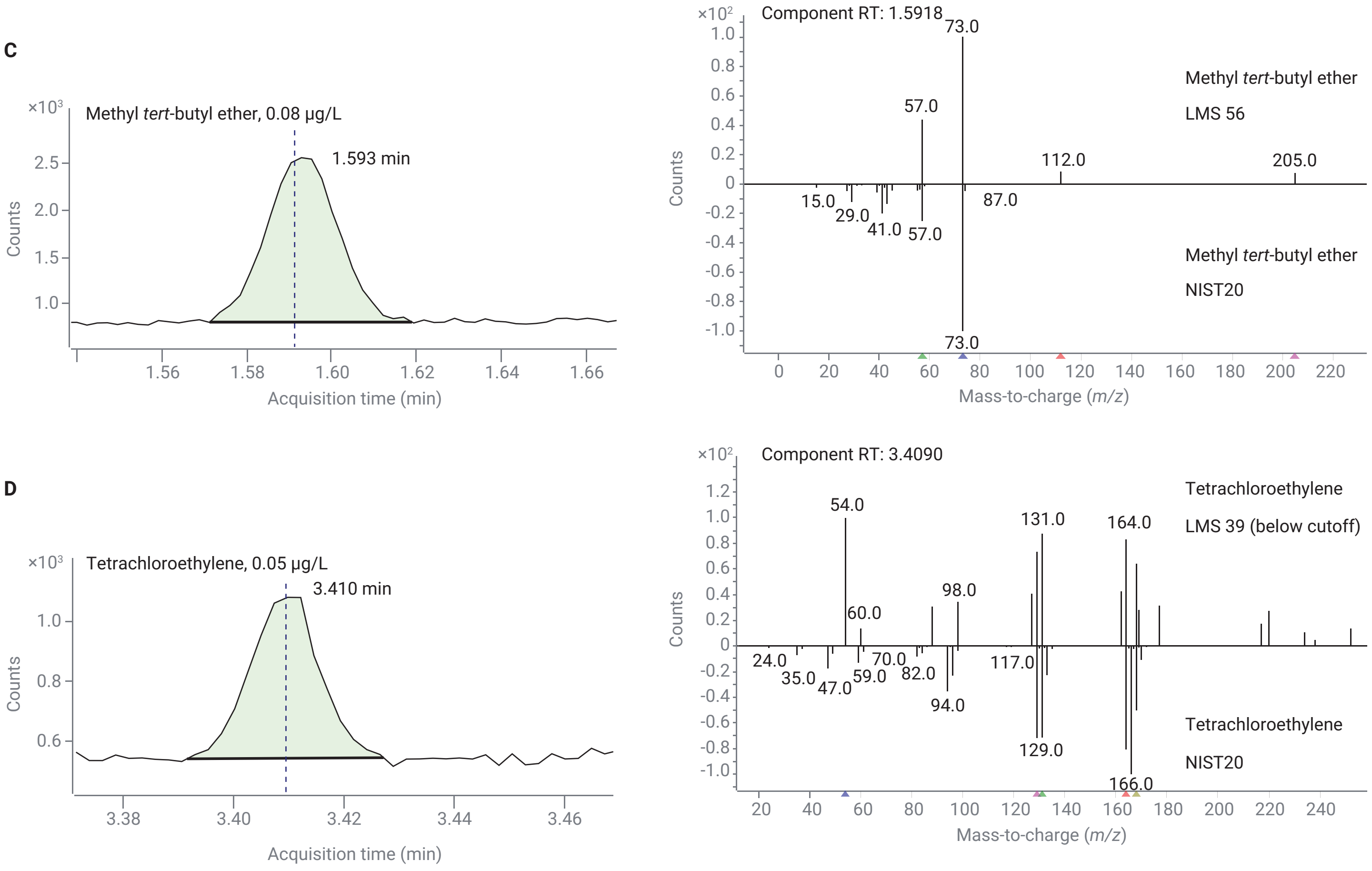


Figure 6. Quantifier ion extracted chromatograms from the SIM run and corresponding deconvoluted spectra from scan runs of the Eastern PA tap water sample (continued on next page).



Conclusion

The Agilent 8890/5977C GC/MSD system coupled with an Agilent 8697 headspace sampler was successfully used with hydrogen carrier gas for the analysis of volatile organic compounds (VOCs) in drinking water. While helium remains the preferred carrier gas for GC/MS, hydrogen has been shown here as a viable alternative if problems with the price and/or availability of helium arise. One of the key components contributing to system performance is the new HydroInert source, which was designed specifically for hydrogen use. In addition to the new source, chromatographic conditions were optimized to provide separation of 80 volatile compounds in 7 minutes.

The results of the scan mode evaluation demonstrated excellent spectral matching against the NIST20 library, and excellent calibration linearity with an average range of 0.16 to 25 µg/L.

The results of the SIM mode evaluation demonstrated excellent calibration linearity with an average range of 0.07 to 25 µg/L, and an average MDL for the 80 compounds of 0.026 µg/L. The method described here gives results comparable to those observed with helium-based headspace methods in references 2 and 3.

The utility of the system was then demonstrated analyzing municipal tap water samples.

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Application Note
Environmental

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 (H_2) 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 H_2 carrier gas.

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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 H_2 in a source. One example is with nitrobenzene, where H_2 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 H_2-related issues and helps improve performance with H_2 carrier gas in GC/MS and GC/MS/MS applications, including SVOC analyses. The HydroInert source with H_2 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 H_2 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 H_2 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	Propyzamide
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	Benz[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-xylenol)	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 H_2 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, H_2 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-d_{10}, 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 H_2 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 H_2 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 H_2 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 R^2 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 8270E[2], measured relative abundance and pass/fail of the relative abundance for the Agilent HydroInert source in a GC/MS/MS system with H_2 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

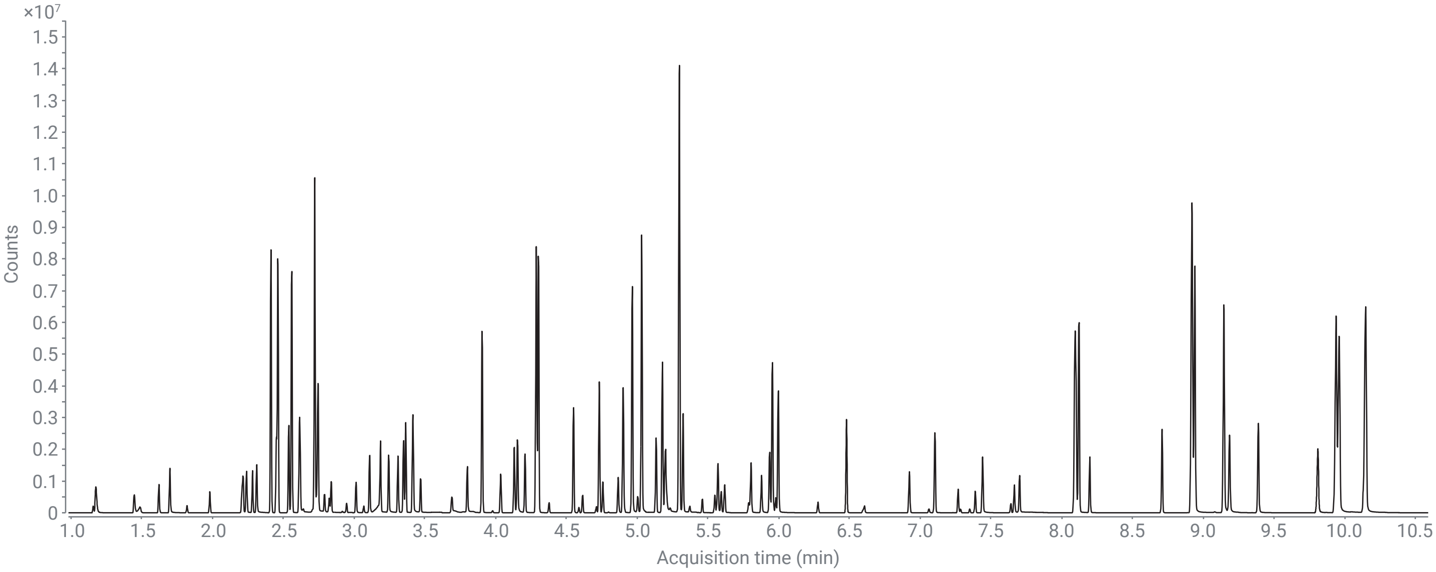

Figure 1. TIC of the 50 µg/mL calibration standard showing separation in under 10 minutes.

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 H_2 carrier gas is the reactivity of H_2 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 H_2 carrier

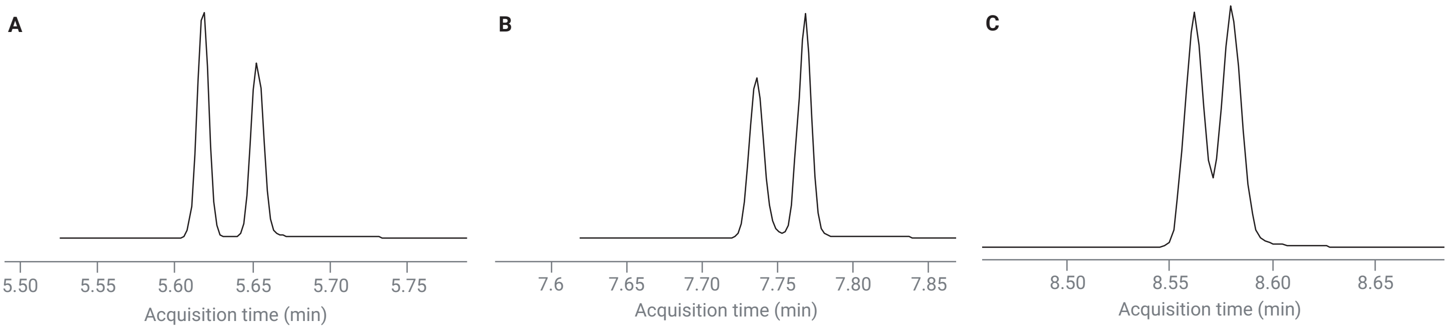

Figure 2. Midlevel standard (5 µg/mL) MRM transition extracted ion chromatograms (EICs) for critical isomer pairs: (A) phenanthrene and anthracene (MRM transition of 178.1 → 152.1 *m/z*); (B) benz[a]anthracene and chrysene (228.1 → 226.1 *m/z*); (C) benzo(b)fluoranthene and benzo(k)fluoranthene (252.1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

gas that they developed with He systems. Retention times and collisions 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 H_2 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 H_2 are not occurring. Missing, very low, or very high MRM transition ratios would indicate reaction with H_2. 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 R^2 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 H_2 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 H_2 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 H_2 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

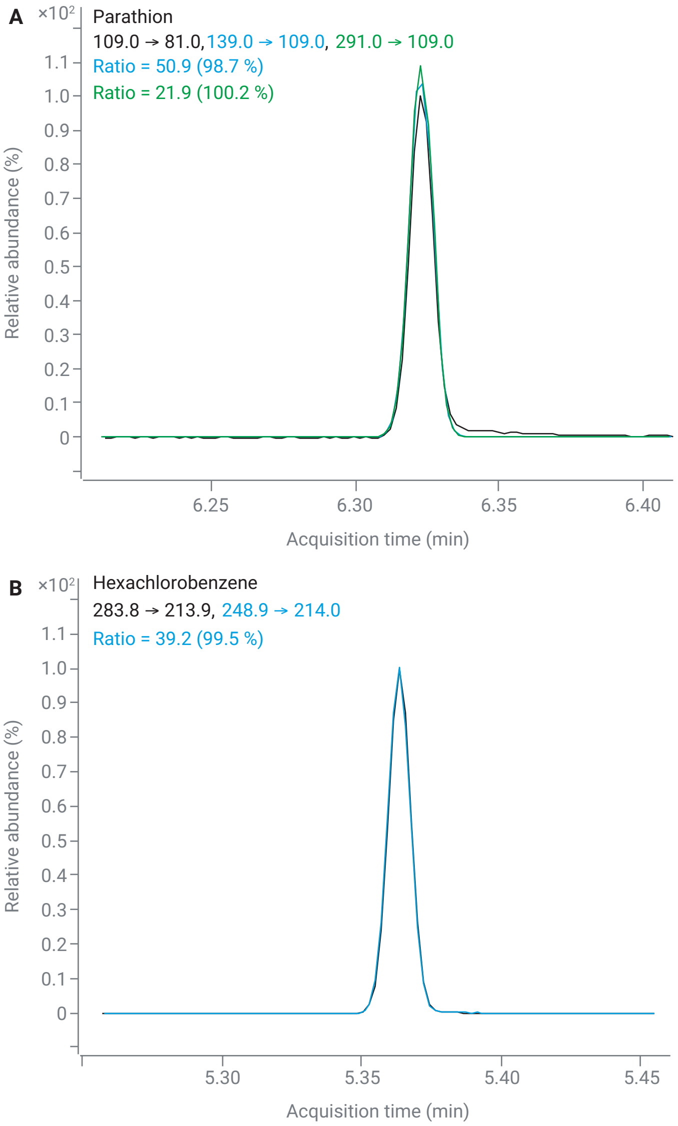

Figure 3. Overlays of MRM transition EICs for (A) parathion and (B) hexachlorobenzene, when using H_2 carrier gas and the Agilent HydroInert source on a GC/MS/MS system, showing retention of key functional groups in the presence of H_2.

Table 5. Initial calibration results for 120 target compounds and surrogates for H_2 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	
p-Phenylenediamine	3.6874	0.232	11.54			0.1	100
N-Nitrosodi-*n*-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-o-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-*n*-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
p-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-*n*-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 H_2 carrier gas with the HydroInert 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 H_2 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 HydroInert source and H_2 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 H_2 data. For 2,4-dinitrophenol, both analyses required linear fits but the H_2 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 H_2 with HydroInert 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 H_2 analysis, while the He results required a linear fit from 5 to 160 µg/mL. Also, benzidine was routinely identifiable in all analyses with H_2 and HydroInert 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 H_2 and HydroInert 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 H_2 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 H_2 carrier gas, HydroInert source, and GC/MS/MS, and no issues with hydrogenation of deuterated compounds. The deuterated surrogate compounds, nitrobenzene-d_5, phenol-d_6, and *p*-terphenyl-d_{14}, 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 H_2 and He data, 80% (60 compounds) had similar or wider calibration ranges for H_2 and HydroInert results. H_2 carrier gas with the HydroInert 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 H_2 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 HydroInert source and H_2 carrier gas. All of these test systems used 9 mm extraction lenses, respective of the source type (e.g. the HydroInert source had a HydroInert 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 H_2 HydroInert 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.

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 HydroInert source and H_2 carrier gas.

Compound	RF from EPA 8270E[4]	RF He GC/MS	RF H_2 and HydroInert 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-*n*-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
2,6-Dinitrotoluene	0.2	0.3	0.03
Di-*n*-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-*n*-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

Repeatability in matrix

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 H_2 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 concertation, 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-*o*-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-*n*-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	*p*-Terphenyl-d_{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	*p*-(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-*n*-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 H_2 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 H_2 carrier gas and the HydroInert source, while retaining mass spectral fidelity and existing MRM transitions for compounds susceptible to H_2 reactivity.

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EPA TO-15 Analysis Using Hydrogen Carrier Gas and the Agilent HydroInert Source

Ambient air testing using cryogen-free thermal desorption and gas chromatography coupled to a single quadrupole mass spectrometer (GC/MS) with hydrogen gas

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Abstract

Ambient air monitoring is commonly analyzed with gas chromatography/mass spectrometry (GC/MS) and helium carrier gas. Recent pressure on the helium supply has required organizations to actively investigate hydrogen carrier gas, but most GC/MS analyses have reduced sensitivity and hydrogenation or dechlorination in the sources. This application note describes the use of hydrogen carrier gas and the Agilent HydroInert source for GC/MS analysis of humidified canister "air toxics" samples at 100% relative humidity (RH), using cryogen-free systems for thermal desorption preconcentration. Detection of 65 target compounds ranging in volatility from propene to naphthalene is demonstrated, with excellent peak shape and performance well within the criteria set out in U.S. Environmental Protection Agency (EPA) method Toxic Organics-15 (TO-15), including method detection limits (MDLs) as low as 11 parts per trillion by volume (pptv).

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Introduction

Monitoring of chemicals in ambient air is necessary to determine the effect they have on the environment and global climate. This monitoring has driven the development of several national and international regulations, primarily in response to increased concern over potentially hazardous volatile organic compounds (VOCs) in ambient (primarily urban) air, industrial emissions, and landfill gas.

Analysis of these VOCs is carried out in accordance with a few standard methods, which require the use of either sorbent tubes (pumped or passive), canisters, or online techniques. Each method has its own advantages and range of applicability, with canister sampling being most popular in the U.S. and China. To achieve the required detection limits using this approach, preconcentration is required to focus analytes and to selectively eliminate bulk constituents. This approach is mandated within the most popular standard method for canisters, U.S. EPA method TO-15.[1]

Despite the popularity of canister sampling, traditional canister preconcentration technologies are challenged by the ever-greater range of analytes and concentrations of interest. The range of temperatures and humidities at sampling locations is also an issue. High levels of humidity are difficult because the ingress of water to the analytical instrument can negatively impact analyte response and repeatability, as well as reduce the lifetime of the column and detector.

The availability of helium has been a concern for several years, and interest in transitioning to alternative carrier gases such as hydrogen has significantly increased. However, existing MS systems have issues with 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 called the Agilent HydroInert source for the Agilent 5977B Inert Plus GC/MSD addresses these hydrogen-related issues and helps improve performance with hydrogen carrier gas in GC/MS. The HydroInert source with hydrogen carrier gas retains mass spectral fidelity and allows users to continue using existing helium-based mass spectral libraries and quantitative methods.

This application note shows how the use of a canister autosampler, an innovative trap-based water removal device, and thermal desorption-gas chromatography/mass spectrometry (TD) GC/MS together with hydrogen carrier gas and the HydroInert source, allow the analysis of a range of volatile "air toxics" from canisters at 100% RH, in accordance with U.S. EPA method TO-15. Note that, although the term "TO-15" is used by some to describe canister sampling in general, the focus of this work will be on compliance with the specific requirements of the method.

Overview of U.S. EPA method TO-15

The key operations are summarized below.

1. **Sampling:** After cleaning and evacuating the canister, it is brought to the sampling site. The canister valve is opened, and a flow controller draws air through a filter into the canister. After the sampling time corresponding to the set constant flow rate is reached, the canister valve is closed and sealed with caps.
2. **Storage:** The sample is kept at ambient temperature and should be analyzed as soon as possible and no later than 20 days after sampling.
3. **Sample analysis:** A known volume of sample is directed from the canister, which is connected to the canister autosampler through a water removal unit and into the multisorbent focusing trap within the concentrator system. The water removal unit will remove most of the water from the sample, and any water vapor remaining in the sample can further be reduced through purging the trap. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and transferred onto a GC column for separation.
4. **Compound identification and quantitation:** Method TO-15 uses GC/MS for qualitative and quantitative analysis of samples. For linear quadrupole MS, monitoring of a wide *m/z* range (scan mode), or ion-selective scanning (SIM mode) patterns can be used to monitor the relevant target compounds. The mass spectra of the individual peaks in the TIC are examined, and VOCs are identified based on the intensities of quantifier and qualifier ions. The acquired mass spectra are then compared with library spectra (taken under similar conditions) to identify the compound. For any given compound, the abundance of the quantifier ion is compared to its abundance for the compound at known concentrations to determine the concentration of the compound in the sample.

Experimental

Instrumentation

The analytical system used for this study was a multigas CIA Advantage-xr canister autosampler with a Kori-xr water removal device and UNITY-xr thermal desorber, coupled to an Agilent 8890B GC and 5977B single quadrupole GC/MSD system with a HydroInert EI source and 6 mm lens (part number G3870-20448).

Tables 1 and 2 display the canister, TD, GC, and MS parameters.

Standard preparation

A 1 part per million (ppm) standard containing 65 "air toxics" compounds at 1 ppm was diluted in 6 L canisters with nitrogen balance gas to 10 parts per billion by volume (ppbv), unless otherwise stated. RH of 100% was achieved by injecting an appropriate volume of water into the canister.

Results and discussion

A listing of results is provided in Table A1 (see Appendix).

Chromatography

Figure 1 shows typical analyses of the 10 ppbv TO-15 standard at 100% RH, and Figure 2 shows extracted ion chromatograms (EICs) for 16 components spanning the volatility range. Note the excellent peak shape, especially for lighter VOCs, which demonstrates the effectiveness of the Kori-xr module at removing water before analyte trapping at 100% RH.

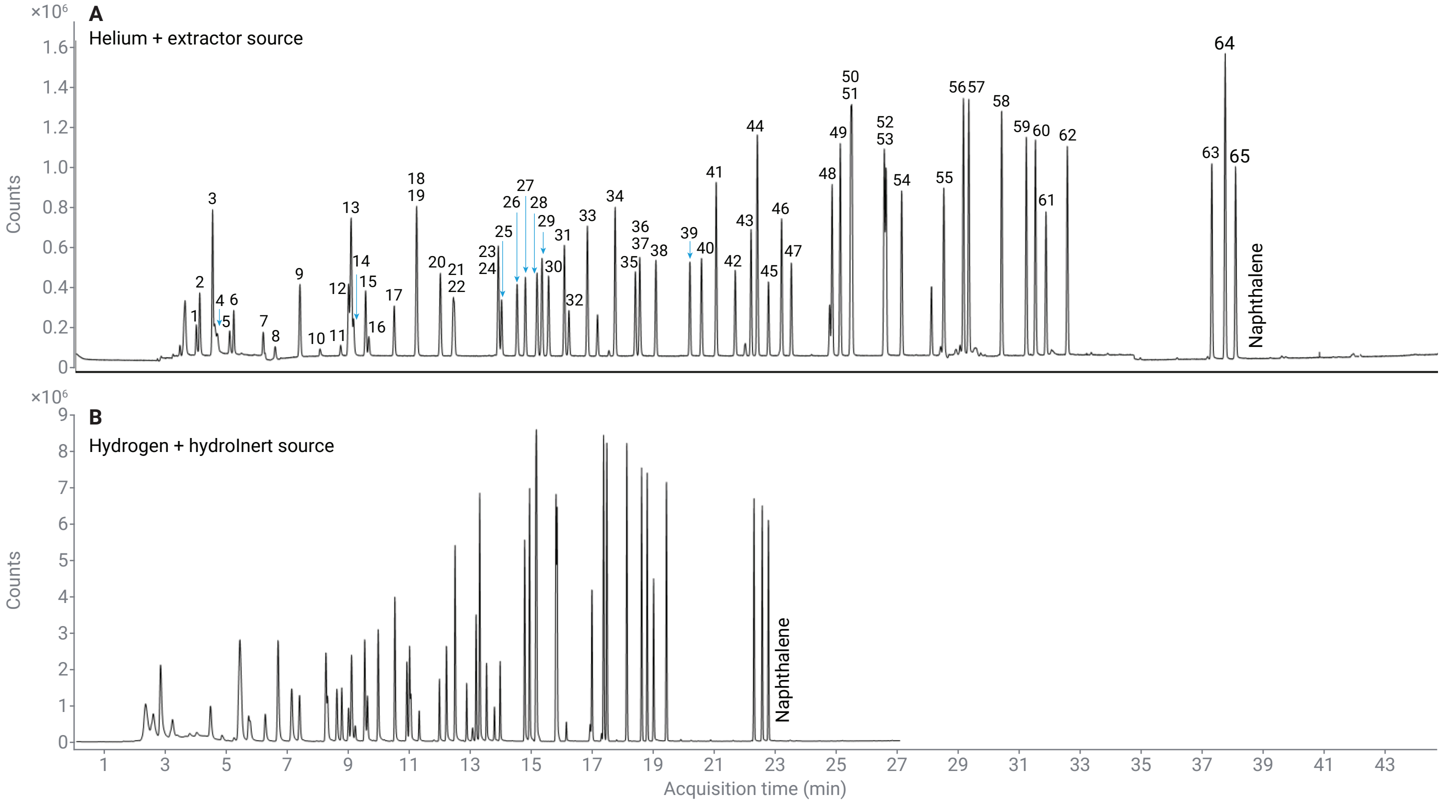
Another noteworthy aspect is that hydrogen carrier gas decreases the GC cycle time by 40% (45 to 27 minutes), as indicated by the shift in naphthalene from 38 to 23 minutes, while maintaining retention time order for all compounds. Faster chromatography can significantly increase sample throughput.

Table 1. GC and TD parameters.

Parameter	Value
Gas Chromatograph	Agilent 8890B GC
Column	Agilent J&W DB-624, 60 m × 0.25 mm, 1.40 µm (p/n 123-1364)
Inlet	Splitless
Inlet Temperature	120 °C
Oven Temperature Program	30 °C (3 min) 8.3 °C/min to 230 °C (0 min)
Total Run Time	27 min
MS Transfer Line Temperature	230 °C
Injection Volume	NA
Carrier Gas	Hydrogen, 2.0 mL/min constant flow
Canister Sampling	
Instrument	CIA Advantage-xr (Markes International)
Sample Volume	Up to 400 mL (for samples of 50 to 100% RH)
Water Removal	
Instrument	Kori-xr (Markes International)
Trap Temperatures	–30 °C/+300 °C
TD	
Instrument	UNITY-xr (Markes International)
Flow Path	120 °C
Standby Split	10 mL/min
Sample Flow	50 mL/min
Trap Purge	1.0 min at 50 mL/min
Trap Desorption	2.0 min at 4 mL/min split flow
Cold Trap	Focusing trap: Air Toxics Analyzer (p/n U-T15ATA-2S)

Table 2. MS parameters.

Parameter	Value
Source	HydroInert source
Mode	Electron ionization, 70 eV
Source Temperature	300 °C
Quadrupole Temperature	200 °C
Scan Range	*m/z* 30 to 300



1. Propene
2. Dichlorodifluoromethane
3. Dichlorotetrafluoroethane
4. Chloromethane
5. Vinyl chloride
6. Butadiene
7. Bromomethane
8. Chloroethane
9. Trichlorofluoromethane
10. Ethanol
11. Acrolein
12. 1,1-Dichloroethene
13. 1,1,2-Trichloro-1,2,2-trifluoroethane
14. Acetone
15. Isopropanol
16. Carbon disulfide
17. Dichloromethane
18. 1,2-Dichloroethene
19. *tert*-Butyl methyl ether
20. Hexane
21. 1,1-Dichloroethane
22. Vinyl acetate
23. *trans*-1,2-Dichloroethene
24. Methyl ethyl ketone
25. Ethyl acetate
26. Chloroform
27. Tetrahydrofuran
28. 1,1,1-Trichloroethane
29. Cyclohexane
30. Tetrachloromethane
31. 1,2-Dichloroethane
32. Benzene
33. Heptane
34. Trichloroethene
35. 1,2-Dichloropropane
36. Methyl methacrylate
37. *o*-Dioxane
38. Bromodichloromethane
39. *cis*-1,2-Dichloropropene
40. 4-Methypentan-2-one
41. Toluene
42. *trans*-1,3-Dichloropropene
43. 1,1,2-Trichloroethane
44. Tetrachloroethene
45. Methyl *n*-butyl ketone
46. Chlorodibromomethane
47. 1,2-Dibromoethane
48. Chlorobenzene
49. Ethylbenzene
50. *m*-Xylene
51. *p*-Xylene
52. *o*-Xylene
53. Styrene
54. Triobromomethane
55. 1,1,2,2-Tetrachloroethane
56. 4-Ethyltoluene
57. 1,3,5-Trimethylbenzene
58. 1,2,4-Trimethylbenzene
59. 1,2-Dichlorobenzene
60. 1,4-Dichlorobenzene
61. Benzyl chloride
62. 1,3-Dichlorobenzene
63. 1,2,4-Trichlorobenzene
64. Hexachlorobutadiene
65. Naphthalene

Figure 1. Analysis of 400 mL of a 10 ppbv 65-component TO-15 standard at 100% RH using helium (A) and hydrogen (B) gas. Naphthalene's retention time shifts from 38 to 23 minutes, indicating a 40% reduction in GC cycle time.

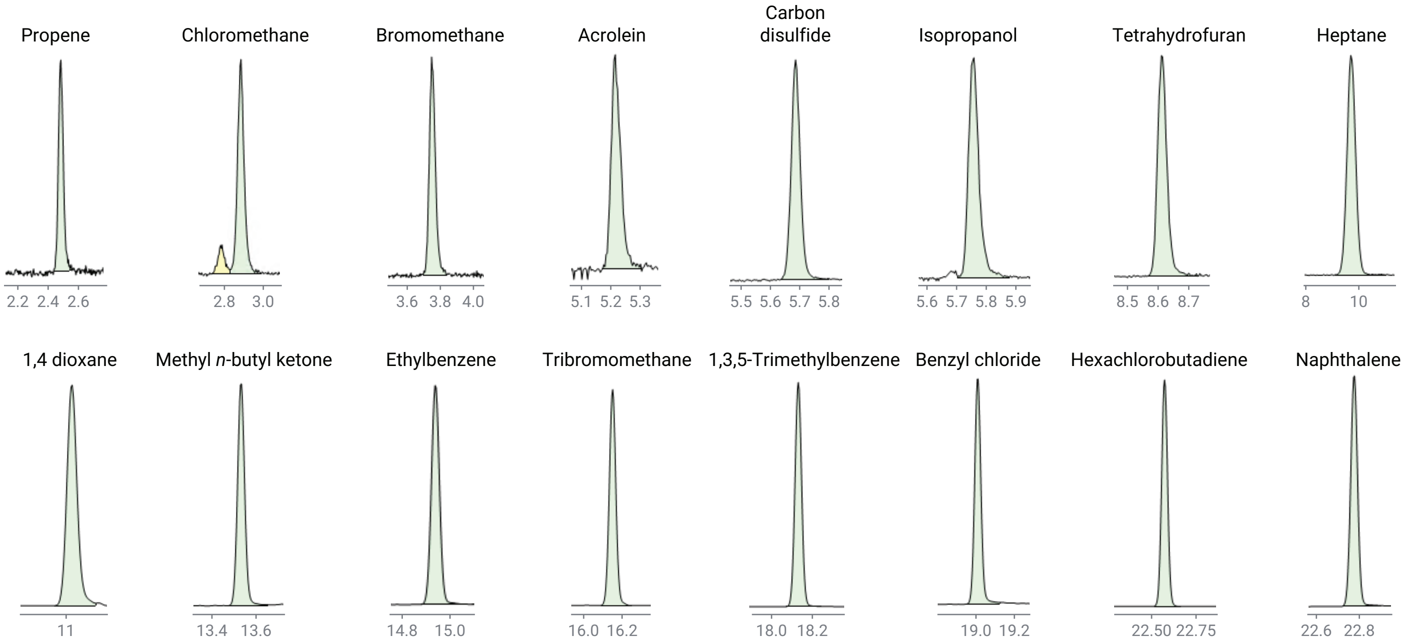


Figure 2. Excellent peak shape of EICs for 16 selected compounds at 2.5 ppbv analyzed using hydrogen gas.

Spectral fidelity

The HydroInert source maintains spectral fidelity by preventing hydrogenation and other reactions that can occur using hydrogen carrier gas. Library match scores (LMS) for all analytes in the 65-component mix were well above 90%, indicating that unwanted source reactions were prevented. Figure 3 shows two examples of high match scores to the National Institute of Standards and Technology helium library (NIST20).

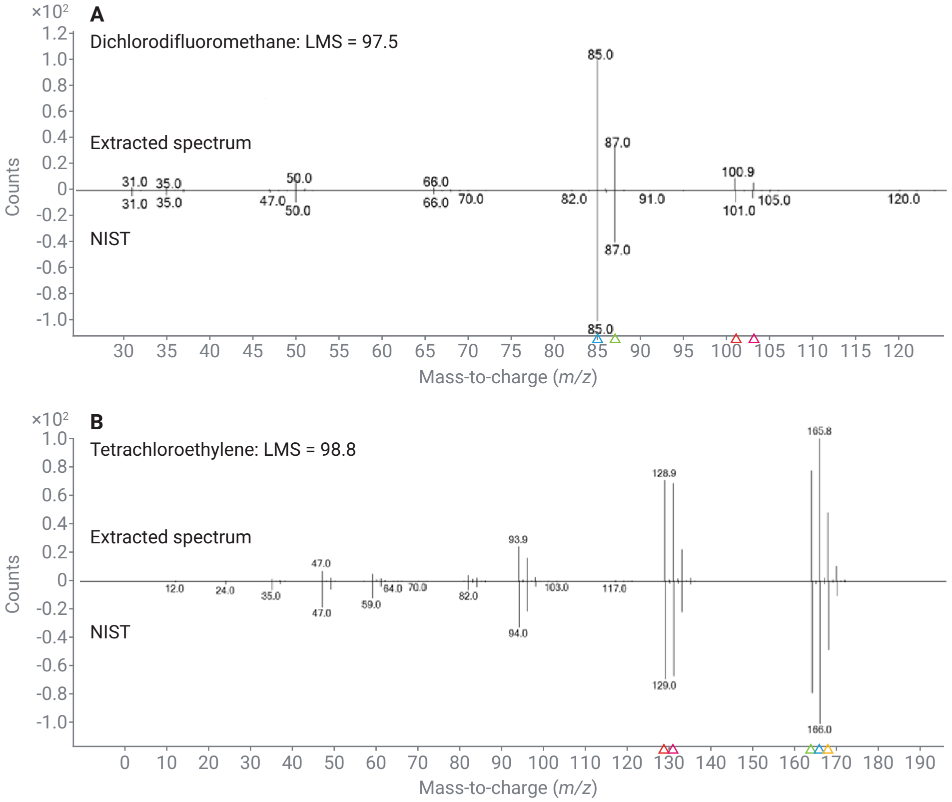


Figure 3. LMS and comparison of extracted versus NIST spectra for dichlorodifluoromethane (A) and tetrachloroethylene (B). Spectral fidelity is maintained.

Linearity

Linearities concerning concentration were calculated at 0.5, 1.25, 2.5, 5, 7.5, and 10 ppbv.

Excellent system linearities were obtained at 100% RH (Table A1), with a mean R^2 value of 0.999 from 0.50 to 10 ppbv. Figure 4 shows a linearity plot for the 100% RH sample, for the set of 14 compounds spanning the volatility range.

Method detection limits

MDLs were calculated based on seven replicate samples at 0.1 ppbv.[2] To comply with Method TO-15, MDLs are required to be ≤0.5 ppbv.

Calculations using hydrogen carrier gas gave a mean MDL of 28 pptv for the 28 compounds analyzed (Table 3), which is well within method criteria confirming that method compliance can be achieved, and exceeded, for TO-15 using the HydroInert source. Values ranged from 11 pptv for 4-ethyltoluene, to 53 pptv for carbon disulfide, with a solitary outlier at 113 pptv for propene. These values are all much lower than the requirement of ≤0.5 ppbv.

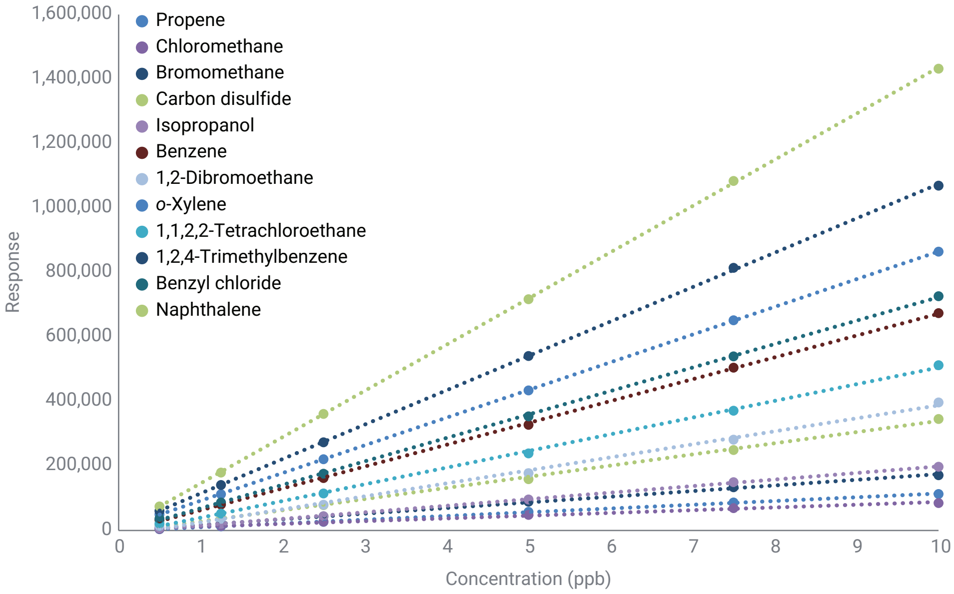


Figure 4. Linearities from 0.5 to 10 ppbv for 14 compounds spanning the range of volatilities, from the 100% RH sample.

Table 3. MDL values for 28 compounds at 0.1 ppbv from the 100% RH sample.

No.	Compound	Hydrogen MDL (pptv)
1	Propene	113
2	Dichlorodifluoromethane	38
3	Vinyl chloride	29
4	Butadiene	33
5	1,1-Dichloroethene	24
6	1,1,2-Trichloro-1,2,2-trifluoroethane	25
7	Carbon disulfide	53
8	Dichloromethane	29
9	tert-Butyl methyl ether	16
10	Vinyl acetate	23
11	Methyl ethyl ketone	42
12	Tetrachloromethane	17
13	Benzene	19
14	Heptane	13

No.	Compound	Hydrogen MDL (pptv)
15	Methyl methacrylate	34
16	Bromodichloromethane	34
17	Toluene	14
18	Tetrachloroethene	13
19	1,2-Dibromoethane	28
20	Chlorobenzene	14
21	Ethylbenzene	14
22	Styrene	23
23	1,1,2,2-Tetrachloroethane	16
24	4-Ethyltoluene	11
25	1,3,5-Trimethylbenzene	14
26	1,2-Dichlorobenzene	17
27	Hexachlorobutadiene	23
28	Naphthalene	50
	Average	28

Reproducibility

Method TO-15 requires that the calculated relative standard deviations (RSDs) for the relative response factors (RRFs) for each compound in the calibration table must be less than 30%, with at most two exceptions up to a limit of 40%. Results were well within the requirements of method TO-15 for 100% RH at 7.47% RSD. Further, for 10 replicates of 10 ppbv at 100% RH, average area RSD was 1.22%. For 50 injections of varying concentrations of 100% RH, average retention time RSD was 0.09%, where criteria state <1% variation (Figure 5). Efficient water management using UNITY-Kori-CIA Advantage-xr enables stable retention times and highly reproducible peak area responses, even with hydrogen carrier gas.

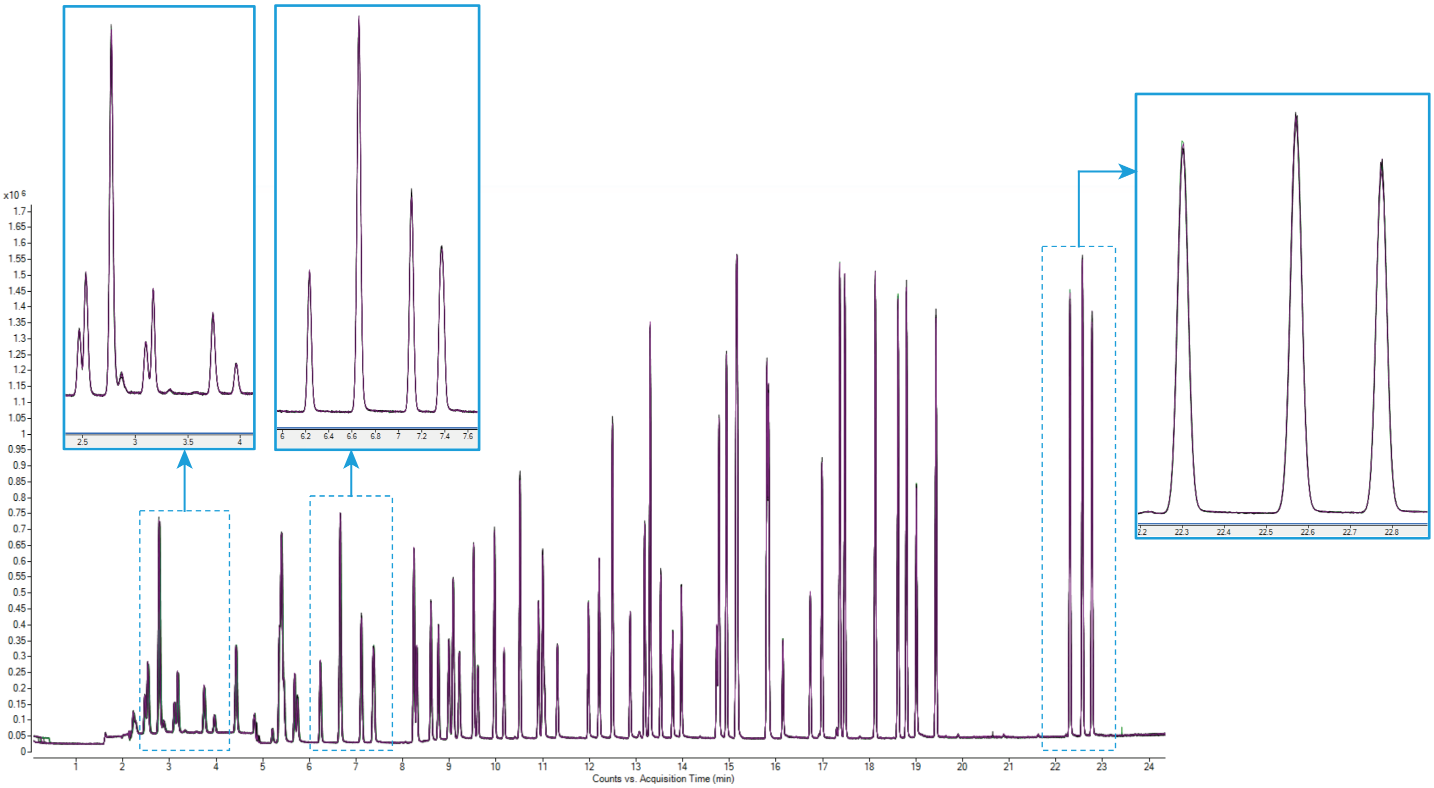
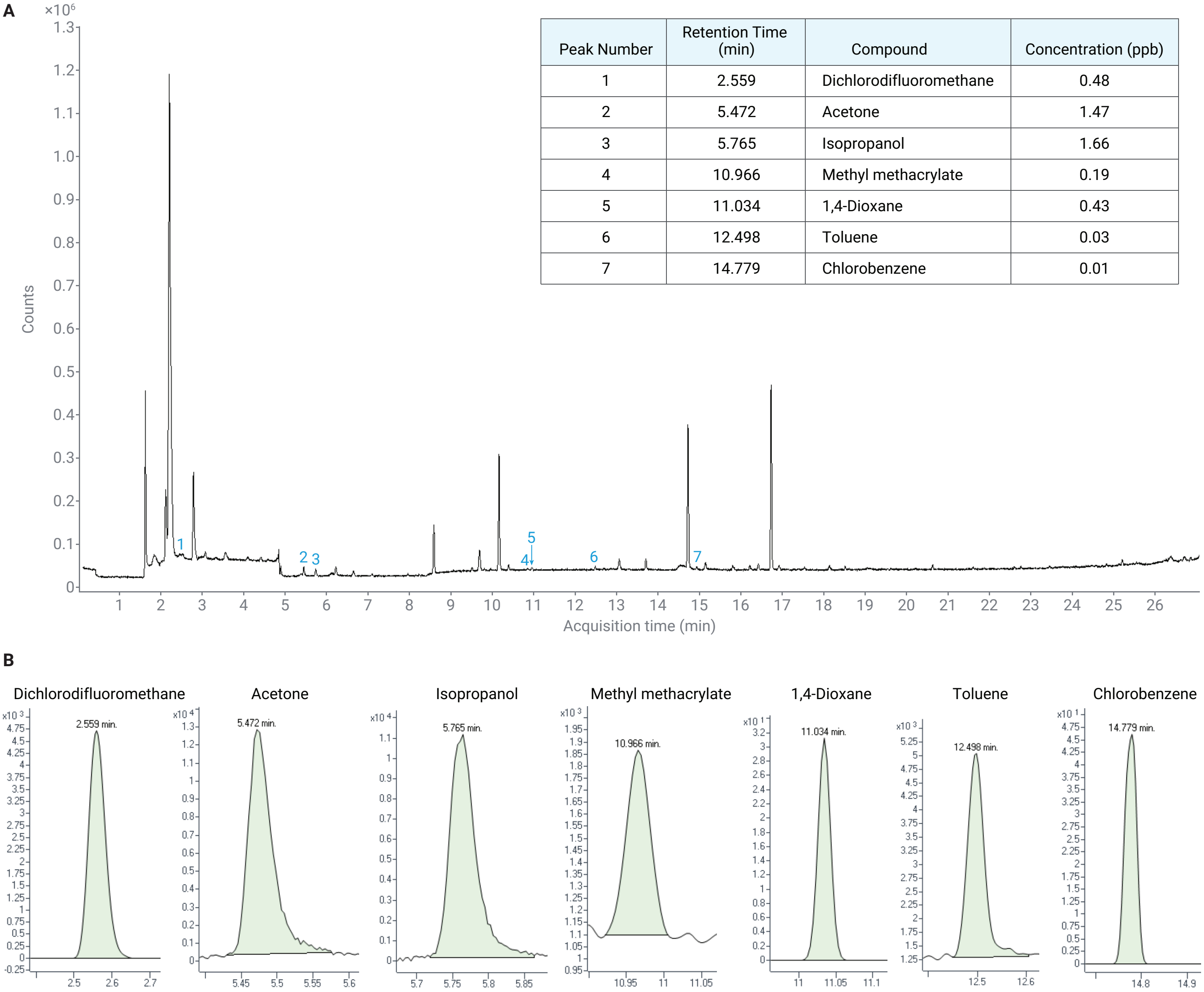


Figure 5. Overlay of 10 replicates at 10 ppbv concentration of 100% RH sample. Average retention time RSD is 0.09%.

Real air sample

To illustrate the performance of the system for a real air sample, 400 mL of lab air was analyzed under the same conditions as described previously. Seven components from the 65-member TO-15 list were found to be at quantifiable levels (Figure 6).



Peak Number	Retention Time (min)	Compound	Concentration (ppb)
1	2.559	Dichlorodifluoromethane	0.48
2	5.472	Acetone	1.47
3	5.765	Isopropanol	1.66
4	10.966	Methyl methacrylate	0.19
5	11.034	1,4-Dioxane	0.43
6	12.498	Toluene	0.03
7	14.779	Chlorobenzene	0.01

Figure 6. (A) Real sample chromatogram generated from analysis of 400 mL of rural air, using the conditions previously described. Compounds from the TO-15 listing are indicated. (B) Zoom of seven compounds detected from the TO-15 list.

Conclusion

The Agilent 8890 GC coupled to the Agilent 5977B single quadrupole MS and CIA Advantage–Kori-xr–UNITY-xr preconcentration system with hydrogen carrier gas allows confident analysis of "air toxics" in humid environments, in accordance with U.S. EPA method TO-15.

Key features of the results are the excellent chromatographic performance for the analysis of a 65-component TO-15 mix (from propene to naphthalene) at 100% relative humidity. Performance was well within the requirements of method TO-15, with method detection limits as low as 11 pptv.

Crucially, this performance has been achieved for even the most volatile of components in the TO-15 mix, due to the efficient and selective removal of water from humid air streams without compromising the analysis of VOCs or polar species. In addition, the system uses electrical trap cooling, eliminating the cost and inconvenience associated with liquid cryogen. The Agilent HydroInert source with hydrogen carrier gas retained mass spectral fidelity, allowing users to continue the use of existing helium-based mass spectral libraries and quantitative methods. The robustness and reliability of the GC/MSD allows long-term operation of the system while generating data in compliance with U.S. EPA TO-15 requirements.

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Appendix

Many conventional systems for canister analysis use liquid cryogen to trap VOCs. Markes' systems instead use electrical (Peltier) cooling, allowing quantitative retention of the most VOCs from large sample volumes, without incurring the cost of liquid cryogen.

Method TO-15 states that any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used.

MDLs were calculated based on 99% confidence for seven values (MDL = 3.143 × standard deviation × concentration).

Table A1. Data comparison of helium and hydrogen carrier gas results obtained for TO-15 standards at 100% RH. Linearity (R^2) values were generated for the concentration range 0.22 to 10 ppbv for analysis with helium carrier gas, and 0.5 to 10 ppv for hydrogen carrier gas.

		Helium Carrier (100% RH)			Hydrogen Carrier (100% RH)		
No.	Compound	RT (min)	RRF RSD (%)	RRF RSD (%)	RT (min)	RRF RSD (%)	RRF RSD (%)
1	Propene	4.894	0.9997	6.3	2.47	0.9994	12.4%
2	Dichlorodifluoromethane	5.032	0.9998	5.6	2.53	1.0000	8.4%
3	Dichlorotetrafluoroethane	5.500	0.9997	7.7	2.77	0.9999	4.2%
4	Chloromethane	5.686	0.9808	11.0	2.88	0.9929	9.3%
5	Vinyl chloride	6.122	0.9994	4.6	3.10	0.9997	10.1%
6	Butadiene	6.276	0.9998	2.0	3.17	0.9999	12.4%
7	Bromomethane	7.346	0.9988	14.4	3.74	0.9988	10.3%
8	Chloroethane	7.723	0.9870	9.1	3.95	0.9999	5.2%
9	Trichlorofluoromethane	8.646	0.9999	6.2	4.42	0.9996	5.6%
10	Ethanol	9.299	0.9997	24.4	4.80	0.9990	20.9%
11	Acrolein	9.925	0.9993	9.3	5.20	0.9988	18.9%
12	1,1-Dichloroethene	10.258	0.9998	1.2	5.35	0.9999	13.2%
13	1,1,2-Trichloro-1,2,2-trifluoroethane	10.337	1.0000	4.8	5.40	0.9998	2.2%
14	Acetone	10.401	1.0000	2.7	5.45	0.9999	5.1%
15	Isopropanol	10.868	0.9981	18.8	5.74	0.9996	14.2%
16	Carbon disulfide	10.884	0.9999	0.9	5.67	0.9984	5.6%
17	Dichloromethane	11.657	0.9998	2.0	6.23	0.9995	8.7%
18	1,2-Dichloroethene	12.461	0.9999	1.6	6.65	0.9997	11.8%
19	*tert*-Butyl methyl ether	12.513	0.9997	4.2	6.65	0.9999	3.4%
20	Hexane	13.285	0.9956	13.6	7.11	0.9999	2.3%
21	1,1-Dichloroethane	13.578	1.0000	5.5	7.36	0.9996	10.1%
22	Vinyl acetate	13.737	0.9998	1.5	7.39	0.9981	12.5%
23	*trans*-1,2-Dichloroethene	15.112	0.9998	3.6	8.24	0.9997	11.4%
24	Methyl ethyl ketone	15.127	0.9998	9.2	8.23	0.9998	6.9%
25	Ethyl acetate	15.314	0.9999	5.5	8.30	1.0000	4.7%
26	Chloroform	15.904	0.9999	5.5	8.76	0.9984	8.6%
27	Tetrahydrofuran	15.912	0.9998	9.2	8.60	0.9997	6.8%
28	1,1,1-Trichloroethane	16.447	0.9999	8.2	8.99	0.9969	7.9%
29	Cyclohexane	16.637	0.9999	8.8	9.08	0.9997	2.6%
30	Tetrachloromethane	16.902	1.0000	7.4	9.21	0.9942	11.1%
31	1,2-Dichloroethane	17.378	1.0000	3.5	9.61	0.9999	5.6%
32	Benzene	17.390	0.9999	6.1	9.52	0.9998	2.0%
33	Heptane	18.075	0.9995	19.0	9.97	0.9998	2.8%
34	Trichloroethene	19.022	0.9999	5.1	10.51	0.9990	10.0%
35	1,2-Dichloropropane	19.557	0.9999	7.1	10.91	0.9990	4.9%
36	Methyl methacrylate	19.822	0.9989	2.9	11.00	0.9997	2.8%
37	*p*-Dioxane	19.914	0.9998	12.6	11.01	0.9981	15.6%
38	Bromodichloromethane	20.227	0.9999	6.2	11.32	0.9953	11.9%
39	*cis*-1,3-Dichloropropene	21.399	1.0000	4.5	11.98	0.9961	12.9%
40	4-Methylpentan-2-one	21.760	0.9999	2.8	12.21	0.9996	5.6%
41	Toluene	22.326	0.9999	16.3	12.50	1.0000	4.1%
42	*trans*-1,3-Dichloropropene	22.810	0.9997	2.9	12.88	0.9973	13.1%
43	1,1,2-Trichloroethane	23.305	1.0000	7.9	13.19	0.9990	6.3%

		Helium Carrier (100% RH)			Hydrogen Carrier (100% RH)		
No.	Compound	RT (min)	RRF RSD (%)	RRF RSD (%)	RT (min)	RRF RSD (%)	RRF RSD (%)
44	Tetrachloroethene	23.828	1.0000	8.8	13.31	0.9996	2.9%
45	Methyl *n*-butyl ketone	23.959	0.9998	2.5	13.53	0.9942	17.0%
46	Chlorodibromomethane	24.398	0.9999	4.7	13.79	0.9973	12.6%
47	1,2-Dibromoethane	24.735	1.0000	4.4	13.98	0.9973	14.2%
48	Chlorobenzene	26.102	1.0000	11.9	14.78	0.9998	2.2%
49	Ethylbenzene	26.407	0.9999	20.2	14.94	1.0000	4.6%
50	*m*-Xylene	26.732	1.0000	20.8	15.16	0.9999	4.7%
51	*p*-Xylene	26.732	1.0000	20.8	15.16	0.9999	4.7%
52	*o*-Xylene	27.837	1.0000	25.2	15.81	1.0000	5.7%
53	Styrene	27.857	0.9999	10.3	15.84	1.0000	4.1%
54	Tribromomethane	28.376	0.9998	4.4	16.15	0.9976	6.8%
55	1,1,2,2-Tetrachloroethane	29.624	0.9999	6.8	16.99	0.9990	8.1%
56	4-Ethyltoluene	30.385	0.9999	6.3	17.37	1.0000	4.1%
57	1,3,5-Trimethylbenzene	30.551	1.0000	19.6	18.13	1.0000	4.5%
58	1,2,4-Trimethylbenzene	31.653	1.0000	10.4	17.48	0.9999	4.6%
59	1,2-Dichlorobenzene	32.485	0.9999	3.9	18.62	1.0000	1.0%
60	1,4-Dichlorobenzene	32.738	0.9999	3.3	18.80	0.9999	2.4%
61	Benzyl chloride	33.107	0.9998	2.3	19.01	0.9998	2.0%
62	1,3-Dichlorobenzene	33.840	0.9999	7.4	19.43	0.9999	3.8%
63	1,2,4-Trichlorobenzene	38.594	0.9965	18.9	22.30	0.9998	2.2%
64	Hexachlorobutadiene	39.121	0.9997	9.4	22.57	0.9988	7.5%
65	Naphthalene	39.315	0.9975	19.7	22.78	1.0000	1.6%
	Mean values		0.9992	8.5		0.9990	7.5%

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Extraction and Analysis of Polycyclic Aromatic Hydrocarbons in Infant Formula

Using Agilent Captiva EMR—Lipid cartridges by GC/MS with hydrogen carrier gas

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Abstract

This application note presents a sample preparation method for the extraction and cleanup of polycyclic aromatic hydrocarbons (PAHs) from infant formula. The use of Agilent Captiva Enhanced Matrix Removal—Lipid (EMR—Lipid) provides highly selective, efficient lipid removal from the infant formula with acceptable analyte recoveries. The solvent exchange to isooctane allows for a favorable GC/MS injection solvent. The application also showcases the use of hydrogen (H_2) carrier gas with the Agilent HydroInert source[1] on the Agilent 8890 GC coupled with the Agilent 5977C GC/MSD.

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Introduction

One of the common ways for humans to encounter PAH exposure is through food consumption. Several countries have drafted legislation to establish tolerable limits for PAHs in foods, food products, and beverages, as well as to enforce monitoring strategies for the most relevant compounds.[2] Furthermore, regulatory agencies such as the World Health Organization (WHO) and the European Commission (EC) have launched regulations to decrease the concentration of PAHs in food, especially through strategies to control the processes that induce their formation.[2]

There is particular concern about the levels of PAHs in infant formula. The EC defines infants as "children under the age of 12 months," and infant formula as "food used by infants during the first months of life and satisfying by themselves the nutritional requirements of such infants until the introduction of appropriate complementary feeding".[3] The current European legislation provides specific PAH parameters for processed cereal-based food and baby food for infants and young children; infant formulae; and follow-on formulae.[4] According to Commission Regulation (EU) number 835/2011, the content of benzo[a]pyrene (BaP) and PAH4 (the sum of BaP, benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), and chrysene (Chr)) in processed cereal-based food and baby food for infants and young children should not exceed 1 µg/kg.

The Captiva EMR–Lipid pass-through cleanup has gained considerable attention since its introduction. The EMR–Lipid sorbent selectively interacts with the unbranched hydrocarbon chains of lipids, leaving "bulky" target analytes in solution for subsequent analysis. This selective interaction mechanism makes it ideal for multiclass, multiresidue analysis in fatty-food matrices.

With the increased global helium (He) crisis in the market, laboratories are looking for a more sustainable alternative to helium and exploring the option of H_2 carrier gas. The economic benefits of H_2 carrier gas for GC are widely known but resulting hydrogenation and dichlorination reactions in the MS source may occur, and thus make the application of H_2 for GC/MS and GC/MS/MS challenging. The Agilent HydroInert source is a newly designed extractor source for GC/MSD that addresses these issues and improves performance with H_2 carrier gas in GC/MS.[1]

This study investigates the analysis of PAHs in infant formula using Captiva EMR–Lipid pass-through cleanup for sample preparation, followed by GC/MS using the HydroInert source and H_2 carrier gas.

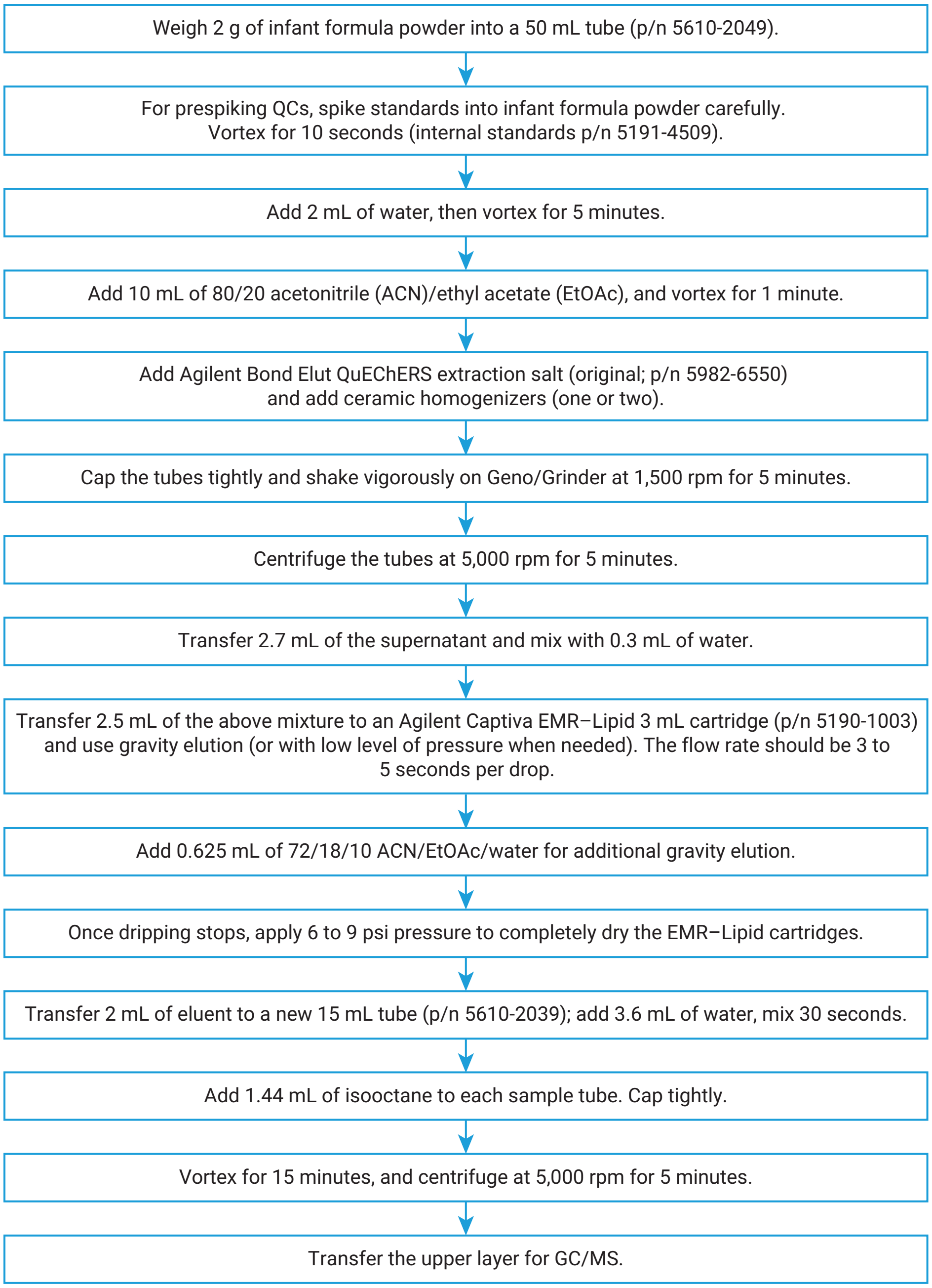
Experimental

Sample preparation

The sample preparation method development followed the previously published PAH method used in beef and salmon.[5] Prior to a solvent extraction, infant formula powder first needs to be dissolved in water. The crude extract can then further be cleaned using Captiva EMR–Lipid 3 mL cartridges. For the analysis of PAHs on the GC/MS, the cleaned extract was back-extracted with isooctane—a more GC-amenable solvent. An outline of the sample preparation procedure is shown in Figure 1. The entire sample preparation procedure introduced a 5× dilution of the infant formula powder sample.

Instrumental analysis

Regarding quantification, PAHs can be quantified using GC/MS. GC/MS allows accurate identification of the target analytes and their respective internal standards with high selectivity, thereby reducing analytical errors.[2] The PAH extraction from infant formula was performed using H_2 and the HydroInert source on the 8890 GC coupled with a 5977C GC/MSD (Figure 2).



Weigh 2 g of infant formula powder into a 50 mL tube (p/n 5610-2049).

For prespiking QCs, spike standards into infant formula powder carefully. Vortex for 10 seconds (internal standards p/n 5191-4509).

Add 2 mL of water, then vortex for 5 minutes.

Add 10 mL of 80/20 acetonitrile (ACN)/ethyl acetate (EtOAc), and vortex for 1 minute.

Add Agilent Bond Elut QuEChERS extraction salt (original; p/n 5982-6550) and add ceramic homogenizers (one or two).

Cap the tubes tightly and shake vigorously on Geno/Grinder at 1,500 rpm for 5 minutes.

Centrifuge the tubes at 5,000 rpm for 5 minutes.

Transfer 2.7 mL of the supernatant and mix with 0.3 mL of water.

Transfer 2.5 mL of the above mixture to an Agilent Captiva EMR–Lipid 3 mL cartridge (p/n 5190-1003) and use gravity elution (or with low level of pressure when needed). The flow rate should be 3 to 5 seconds per drop.

Add 0.625 mL of 72/18/10 ACN/EtOAc/water for additional gravity elution.

Once dripping stops, apply 6 to 9 psi pressure to completely dry the EMR–Lipid cartridges.

Transfer 2 mL of eluent to a new 15 mL tube (p/n 5610-2039); add 3.6 mL of water, mix 30 seconds.

Add 1.44 mL of isooctane to each sample tube. Cap tightly.

Vortex for 15 minutes, and centrifuge at 5,000 rpm for 5 minutes.

Transfer the upper layer for GC/MS.

Figure 1. Infant formula sample preparation procedure chart.

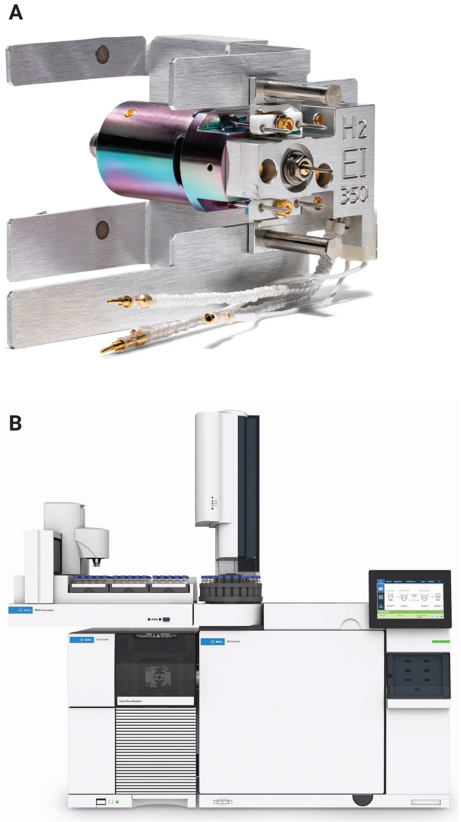


Figure 2. Agilent HydroInert source (A) and Agilent 8890 GC and 5977C GC/MSD system (B).

The 8890 GC system was configured with an Agilent J&W DB-EUPAH GC column (part number 121-9627) combined with an Agilent 5977C Inert Plus GC/MSD with a HydroInert source. Tables 1 and 2 summarize the GC/MS instrumentation and consumables used in this study.

Table 1. GC and MSD instrumentation and consumables.

Part	Description
GC	Agilent 8890 GC system
MS	Agilent 5977C Inert Plus GC/MSD
Source	Agilent HydroInert source with 9 mm HydroInert extraction lens
Syringe	Agilent Blue Line autosampler syringe, 10 µL, PTFE-tip plunger (p/n G4513-80203)
Column	Agilent J&W DB-EUPAH GC column, 20 m × 0.18 mm, 0.14 µm, 7-inch cage (p/n 121-9627)
Inlet Liner	Agilent inlet liner, Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)

Table 2. GC and MSD instrument conditions.

Parameter	Value
Injection Volume (L1)	2 µL
Injection Type	Two-layer sandwich (L1, L2)
L1 Air Gap	0.2 µL
L2 Volume	0.5 µL (used for internal standard sandwich injection)
L2 Air Gap	0.2 µL
Inlet Temperature	320 °C
Inlet Mode	Pulsed splitless
Septum Purge Flow	3 mL/min
Septum Purge Flow Mode	Switched
Injection Pulse Pressure	40 psi until 0.75 min
Purge Flow to Split Vent	50 mL/min at 0.7 min
Column Temperature Program	60 °C (1 min hold); 60 °C/min to 180 °C (hold 0 min); 3 °C/min to 335 °C (hold 15 min)
Carrier Gas and Flow Rate	H_2, 0.9 mL/min constant flow
Transfer Line Temperature	320 °C
Ion Source Temperature	320 °C
Quadrupole Temperature	150 °C
Data Acquisition	Selective ion monitoring (SIM)
Tune	etune.u
Gain Factor	5

Results and discussion

Sample preparation

Low regulatory limits and food matrices add layers of complexity to the analysis of PAHs. As a result, extensive, multistage sample preparation methods are usually necessary. Several factors can affect the quantification of PAHs, such as solubility, temperature, ionic strength, interactions with the matrix of origin, and so on. PAHs are highly hydrophobic compounds, especially heavy PAHs with three or four rings, which typically bear high log P values above 5. Therefore, they are easily accumulated in matrices with high lipid content or other nonpolar components.[6] Accordingly, each food matrix has a specific sample preparation according to its composition. Thus, in-depth knowledge of the matrix of interest is essential for determining the appropriate steps for PAH analysis.[7]

Infant formula is a relatively fatty food matrix, containing 5 to 20% fat. The dry powder must be dissolved in water before solvent extraction. After solvent extraction from the infant formula matrix, a cleanup/purification step is essential to isolate the analytes of interest and to remove potential interferences, especially fatty co-extractives such as triglycerides and fatty acids, where Captiva EMR–Lipid can provide an efficient matrix cleanup.[2]

The use of 20/80 EtOAc/ACN solvent for extraction provides enough strength to extract hydrophobic PAHs from fatty matrices. The additional elution on Captiva EMR–Lipid assures the complete elution of targets from Captiva EMR–Lipid cartridges during pass-through cleanup. The isooctane back extraction after cleanup makes it easier to switch from the extraction solvent to a more GC-amenable solvent and provides partial sample concentrating.

For infant formula powder, it is important to dissolve the dry powder first to achieve efficient solvent extraction. The addition of water to dissolve the infant formula powder was investigated by comparing a higher water volume of 10 mL to the lower volume of 2 mL. Figure 3 shows the target-recovery comparison using the two different water-addition volumes. The results clearly demonstrated that the lower water volume (2 mL) for powder dissolving played a significant role in heavy-PAH recoveries. This is because the higher water volume (10 mL) can result in the reduced solubility of more hydrophobic PAHs and cause target losses during extraction. As a result, the 2 g of infant formula was dissolved into 2 mL of water for the following solvent extraction.

Analytical system

Due to recent helium supply shortages, required organizations have had to investigate the use of H_2 carrier gas. However, most GC/MS analyses have reduced sensitivity and hydrogenation or dechlorination in the source.

A GC/MS total ion chromatogram (TIC) scan of the infant formula blank is shown in Figure 4. The full scan of the blank matrix displays the sample matrix chromatographic background baseline. A matrix blank was used for postspiking standard samples.

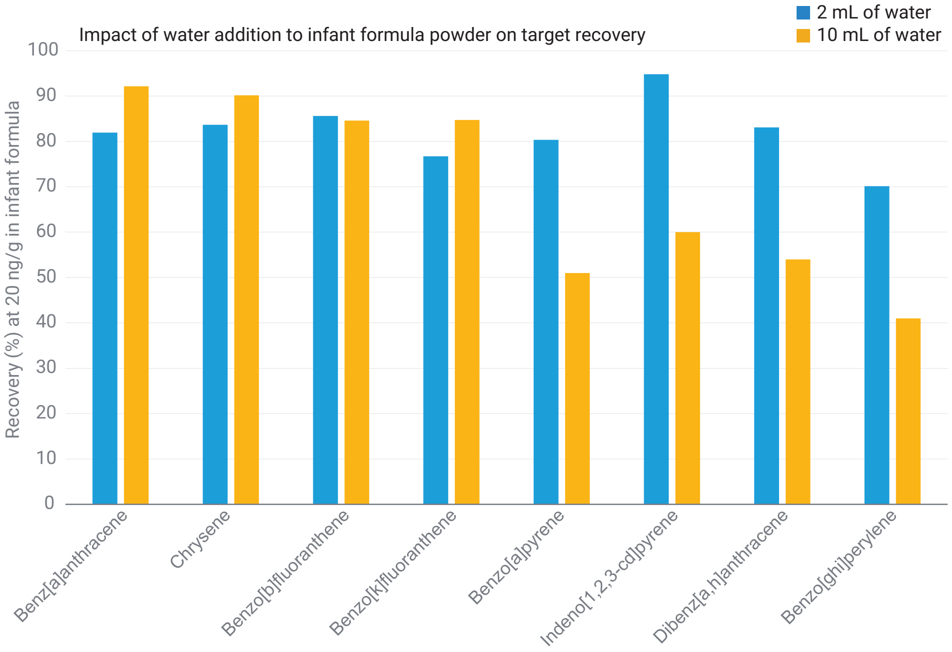


Figure 3. Comparison of PAH target recoveries for different water volumes used to dissolve infant formula before solvent extraction.

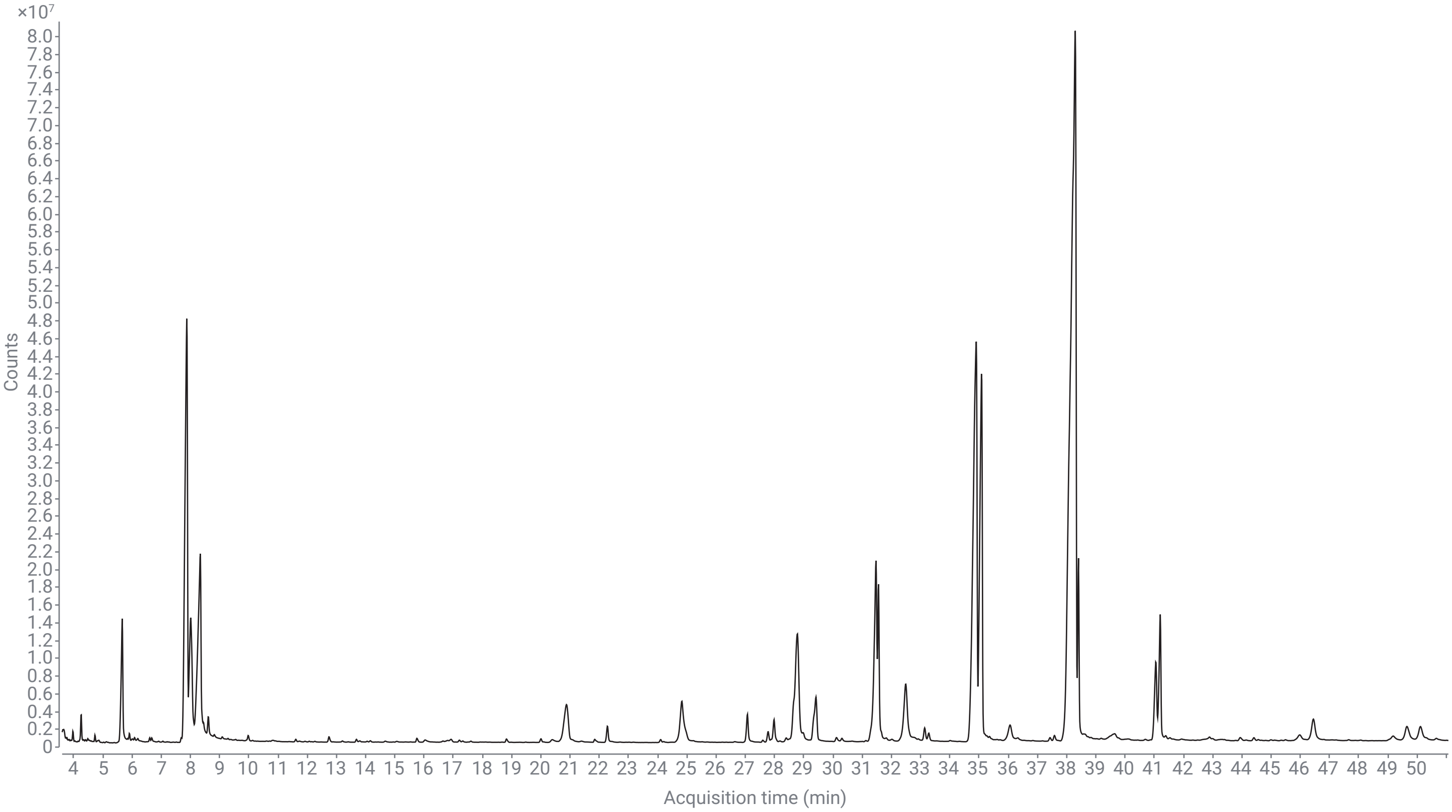


Figure 4. GC/MS TIC scan of infant formula matrix blank.

For quantitation of PAHs in infant formula, a matrix-matched calibration was used with seven calibration levels from 0.1 to 20 ppb in vial (0.5 to 100 µg/kg in infant formula). Target analyte retention times (RTs) and linearity values are displayed in Table 3. Acquiring a quantitation level below 1 µg/kg for BaP and PAH4 allows accurate quantitation for the Commission Regulation (EU) number 835/2011.

Method recovery and reproducibility

The examination of prespiked samples allowed the evaluation of the developed quantitation method performance. A GC/MS SIM chromatogram of target PAHs in a postspiked infant formula sample (1 ng/g in the infant formula extract) is shown in Figure 5.

Table 3. Analysis data for target PAHs.

Compound	RT	Linearity	Quantifier Ion (*m/z*)	Qualifier Ion 1 (*m/z*)	Qualifier Ion 2 (*m/z*)
Benzo[a]anthracene-d12	19.00		240.1	236.1	
Benz[a]anthracene (BaA)	19.15	0.999	228	226	229
Chrysene-d12	19.50		240	236	
Chrysene (Chr)	19.69	0.997	228.1	226.1	229
Benzo[b]fluoranthene-d12	26.50		264	260	
Benzo[b]fluoranthene (BaF)	26.67	0.998	252	250	253
Benzo[k]fluoranthene-d12	26.70		264.1	260.1	
Benzo[k]fluoranthene	26.85	0.994	252	250	253
Benzo[a]pyrene-d12	29.14		264.1	260.1	
Benzo[a]pyrene (BaP)	29.31	0.995	252.1	250.1	248
Indeno[1,2,3-cd]pyrene-d12	35.91		288	284	
Indeno[1,2,3-cd]pyrene	36.05	0.998	276	274	277
Dibenzo[a,h]anthracene-d14	36.14		292	288	
Dibenz[a,h]anthracene	36.35	0.998	278.1	276.1	279.1
Benzo[ghi]perylene-d12	37.71		288	287	
Benzo[ghi]perylene	37.86	0.997	276.1	274.1	277
Dibenzo[a,i]pyrene-d14	46.45		316	317	

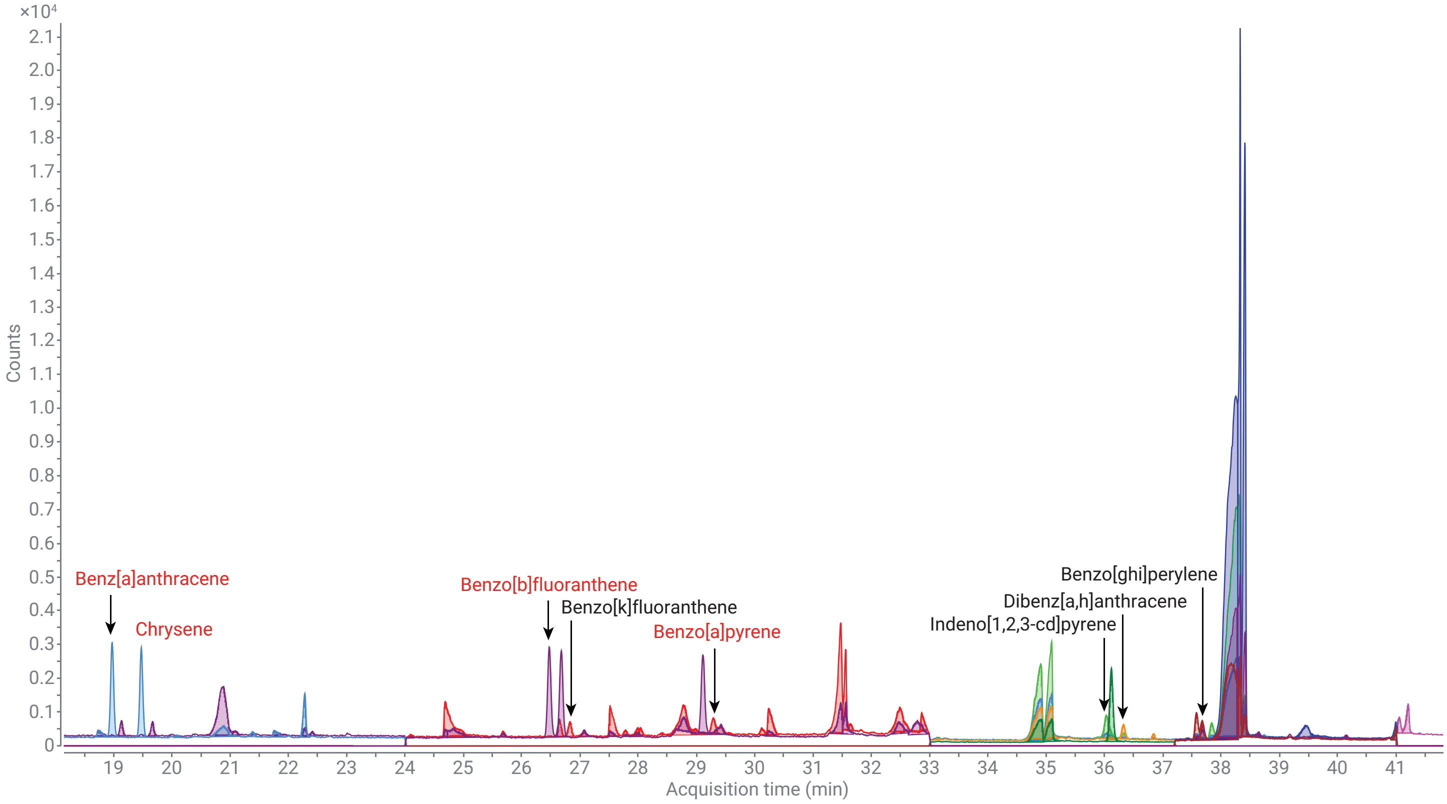


Figure 5. GC/MS SIM chromatogram of PAHs in a postspiked infant formula sample (1 ng/g in the infant formula extract).

Target analyte recoveries for eight PAHs were calculated based on the direct peak-area comparison of the prespiked and postspiked infant formula samples, and the results are shown in Figure 6. The four critical PAH compounds—BaP, BaA, BbF, and Chr—are in red.

Three levels of spiked samples were used for method recovery and reproducibility validation, which included 1, 10, and 50 ng/g in infant formula with six replicates at each level.

The results confirmed that the method delivered acceptable >60% recoveries (60 to 95%) with <20% RSD, except for benzo[k]fluoranthene at 1 ng/g level (54% recovery), and benzo[ghi]perylene (34.6% RSD). The two outliers are mostly due to the low sensitivity of the instrument detection method and more matrix impact at the 1 ng/g level. The instrument method sensitivity and matrix impact to low-level spiked samples also resulted in higher RSDs at the 1 ng/g level.

Conclusion

This application note presents a sample preparation method using solvent extraction followed by Agilent Captiva EMR—Lipid pass-through cleanup for PAH analysis in infant formula. The study also showed that the use of the Agilent HydroInert source with H_2 carrier gas on the Agilent 8890 GC and 5977C GC/MSD system can be used for the determination of PAHs at low concentrations. The method delivered acceptable recovery, reproducibility, and quantitation results that meet the EU regulation for PAH analysis in food.

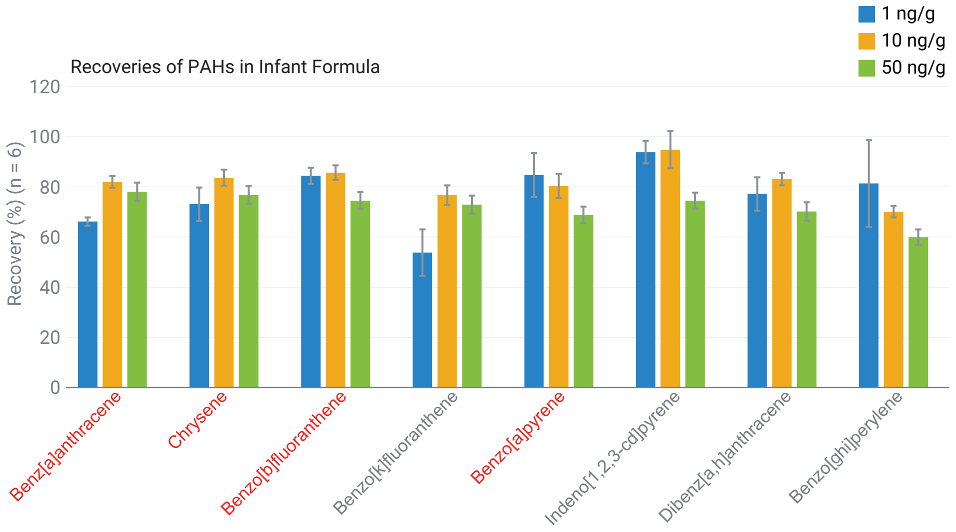


Figure 6. Method recoveries and reproducibility for targeted PAHs in infant formula.

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Robust, Sensitive, and Reliable ACCUTRACE^{TM} Plus Fuel Marker Analysis by Two-Dimensional GC/MS Using Hydrogen as the Carrier Gas

Authors

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Abstract

Fuel marking is an authentication method used by governments to ensure that the national fuel supply comes from a legal source and complies with the regional standards. It is necessary to have a solid method to deter illegally traded fuel. At the same time, laboratories are reducing their helium dependence due to its high cost and they desire methods that use alternative carrier gases without sacrificing chromatographic performance.

This application note demonstrates the analysis of a newly introduced fuel marker in diesel fuel by two-dimensional GC/MS with the use of hydrogen as the carrier gas. A capillary flow technology (CFT) Deans switch is used to provide a robust and sensitive analytical solution for the detection and quantitative analysis of the fuel marker. It allows analysis down to low mg/L levels by direct injection of diesel fuel, to comply with all regional regulations.

Introduction

Tax avoidance can cause governments to lose enormous sums of money every year. There are many forms of tax avoidance, including avoiding paying tax on commodities such as fuel. In different countries, fuel designated for agricultural use in farm vehicles and machinery, for example, as well as fuel oil for heating purposes, attracts a lower tax duty rate than fuel designated for use in road vehicles. Lower-tax fuels are "marked" with different combinations of colored dyes to identify them clearly. It is a criminal offence to use different fuels than the ones allowed for specific vehicles.[1]

The European Commission has established a common fiscal marker for gas oils and kerosene. Its commercial name is ACCUTRACE™ Plus, developed by a worldwide leading chemical company, and it contains butoxybenzene as the preferred marker. The European Commission also states that every member shall set a marking level of this new marker to be at least 9.5 mg of butoxybenzene per liter, and not more than 14.25 mg of butoxybenzene per liter of energy product.[2]

Experimental

Chemical and reagents

- Butoxybenzene (CAS registration number 1126-79-0) and all solvents were purchased from VWR, Germany. Unmarked diesel was purchased directly from a local petrol station.
- All standards were prepared and diluted in *m*-xylene.
- All the analyses were carried out using hydrogen as the carrier gas.
- A six-point calibration curve was prepared from pure butoxybenzene at the following concentrations: 0.05, 0.1, 0.2, 0.5, 1.0, and 10 mg/L.

Instruments and method

An Agilent 8890 GC system, including:

- Split/splitless inlet
- Flame ionization detector
- Pneumatic switching device (PSD)
- Deans switch
- Agilent J&W DB-17ht GC column, 15 m × 250 µm, 0.15 µm
- Agilent J&W DB-WAXetr GC column, 30 m × 250 µm, 0.5 µm

An Agilent 5977B GC/MSD, including:

- Extractor source
- Extractor lens, 9 mm
- SIM mode for *m/z* 94 and 150, with a 100-millisecond dwell time

All the method parameters are available in Table 1.

Table 1. GC/MS method.

Agilent 8890 GC system			
Oven	°C/min	Hold (°C)	Hold (min)
		100	1
	10	165	0.5
	30	240	0.5
Inlet (Split/Splitless)			
Liner	p/n 5190-2295		
Temperature	250 °C		
Mode	Split		
Split Ratio	70:1		
Column 1			
Column	Agilent J&W DB-17ht, 15 m × 250 µm, 0.15 µm (p/n 122-1811)		
Mode	Ramped flow		
Column 1 Flow Settings	Rate	Flow	Hold Time
		1 mL/min	4 min
	100 mL/min	−2 mL/min	End of the run
Column 2			
Column	Agilent J&W DB-WAXetr, 30 m × 250 µm, 0.5 µm (p/n 122-7333)		
Mode	Constant pressure		
Pressure	9.7 psi		
Column 3			
Retention Gap	0.48 m, 100 µm, 0 µm		
Mode	Constant pressure		
Pressure	9.7 psi		
Deans Switch			
Time (min)	Setpoint		
3.68	On		
3.78	Off		
Agilent 5977B GC/MSD			
Acqusition Mode	SIM		
Gain Factor	1		
SIM Ions			
m/z	Dwell Time		
94	100		
150	100		

Deans switch setup

The use of the CFT Deans switch is critical to providing the robust analytical performance required for this fuel marker analysis. The Deans switch provides a two-dimensional GC method (often referred to as "heart cutting"). It diverts the bulk of the diesel fuel to the FID and only a small portion of the chromatogram (the heart cut time window), in which the marker chemical elutes and is transferred to a second column, with different polarity, and is analyzed by the MSD. By design, the MS ion source is only exposed to a very small amount of the diesel fuel with each injection, and that is the small amount of matrix that elutes along with the marker compound. After the marker compound has eluted, the system uses a postrun backflush to remove any remaining high boilers from the primary column. The four stages of the Deans switch operation are shown in Figures 1 to 4.

In the default stage, the primary column effluent (DB-17ht) is diverted to the FID via a restrictor column, as shown in Figure 1. During the heart cut, the Deans switch valve is operated (Figure 2), and the outlet of the primary column is sent to the secondary column (DB-WAXetr). On this column, with another phase, butoxybenzene is further separated from the diesel matrix. After the heart cut time, the Deans switch valve position is changed again, so the primary column effluent is sent to the FID. The advantage of the Agilent Deans switch setup with PSD is that concurrent backflushing of the primary column can be done while the separation of the butoxybenzene is still going on in the secondary column (Figure 4). Concurrent backflushing reduces overall analysis time since there is no waiting for the remaining sample matrix to elute from the primary column.

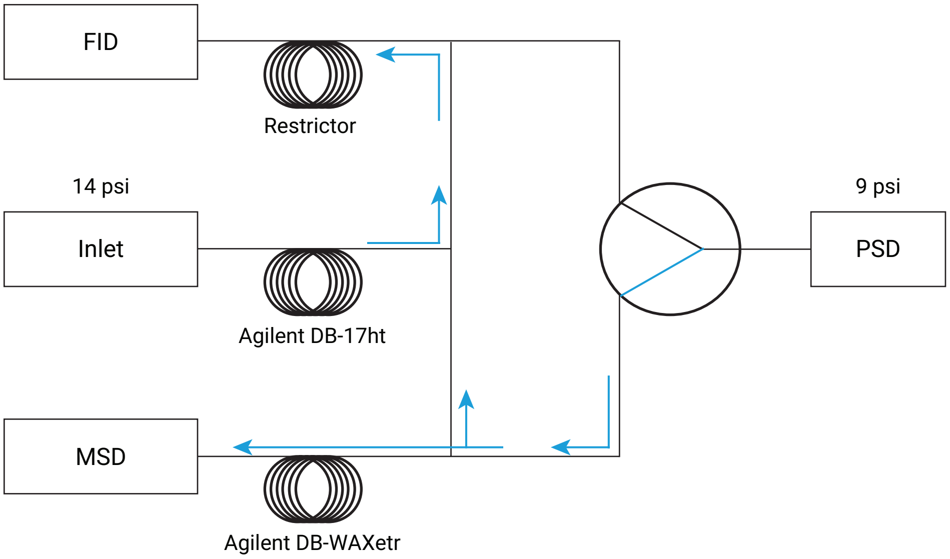


Figure 1. Primary column effluent diverted to the FID.

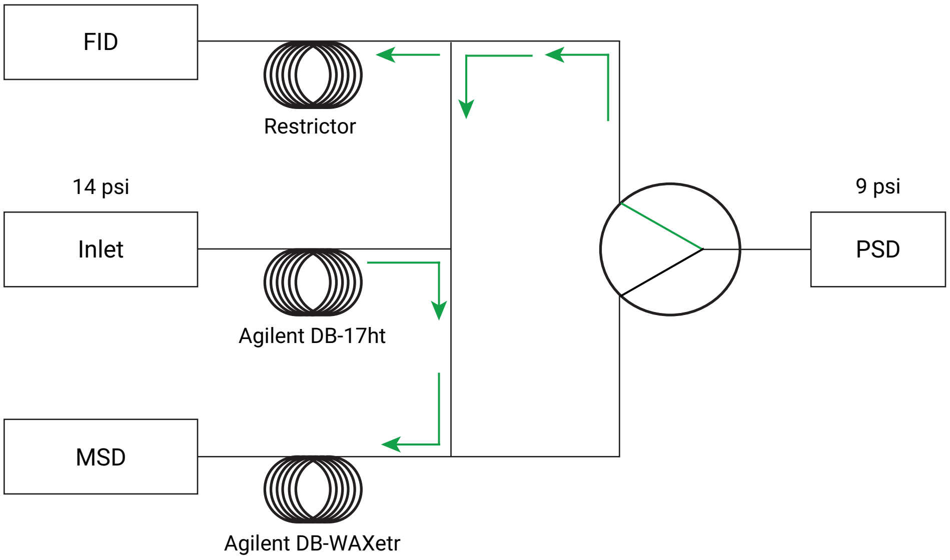


Figure 2. Primary column effluent diverted to the MSD.

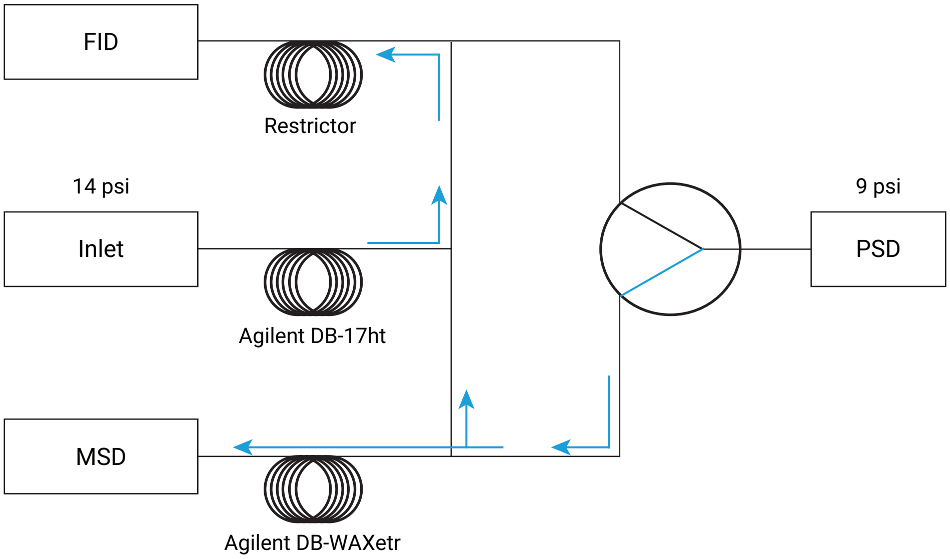


Figure 3. Primary column effluent diverted back to the FID.

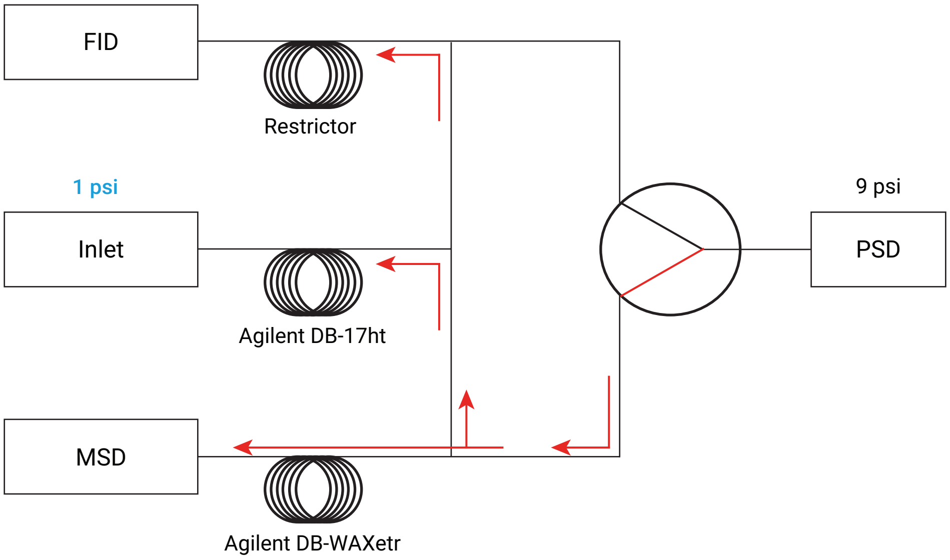


Figure 4. Concurrent backflush. Inlet pressure is dropped to 1 psi, and the heavier boilers are pushed backward into the inlet and out through the split vent line.

To reduce the amount of matrix that is diverted to the MSD, it is important to select the narrowest possible heart cut window. This ensures not only the best resolution of the compound of interest on the second column but also keeps the MSD source protected from such a high level of possible contamination. A chromatogram showing the selection of the cut window is visible in Figure 5.

Optionally, as soon as butoxybenzene is on the second column, it is possible to activate a concurrent backflush, by dropping the pressure on the inlet. This feature reduces the amount of matrix reaching the detectors and helps shorten the total run time.

Calibration

The calibration was carried out at six different concentrations between 0.05 and 10 mg/L to show that the trace-level detection capabilities of the system are also suitable for quantifying the marker even when blended with unmarked fuel (Figure 6).

The method shows a linear regression of 0.99998, with accuracies always below 10% for all the calibration points, as shown in Table 2.

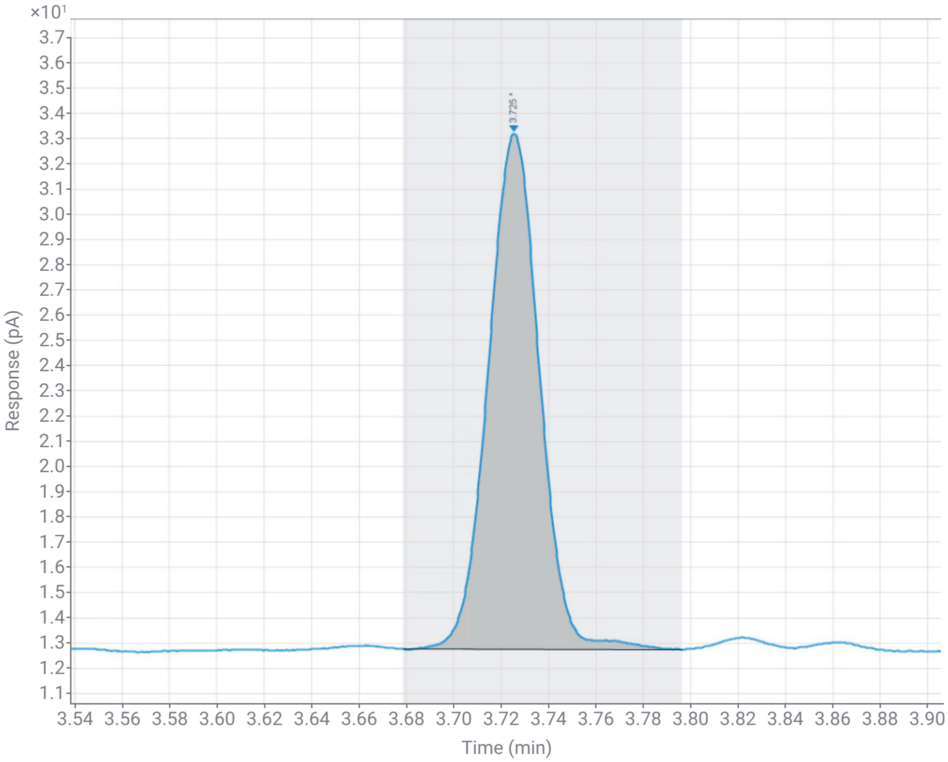
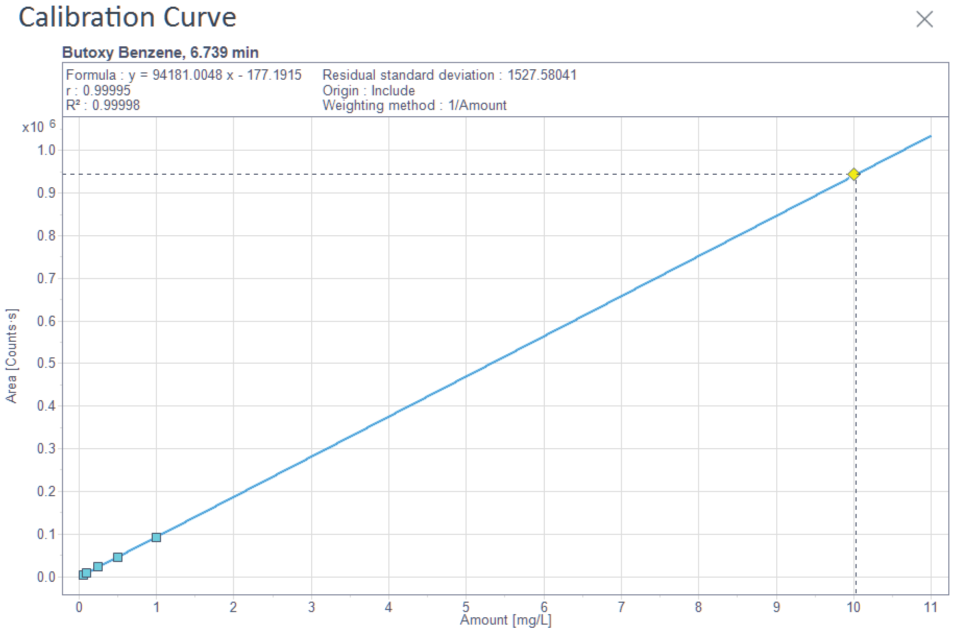


Figure 5. The heart cut window is set based on injection with the Deans switch in the off position. From this chromatogram, the window is set to be between minutes 3.68 and 3.76.


Calibration Curve

Butoxy Benzene, 6.739 min

Formula : y = 94181.0048 x - 177.1915
r : 0.99995
R² : 0.99998
Residual standard deviation : 1527.58041
Origin : Include
Weighting method : 1/Amount

Figure 6. Calibration curve for butoxybenzene.

The method had also been tested for reproducibility in matrix analysis by injecting spiked diesel with an unknown amount of butoxybenzene 20 times (Figure 7). With an average concentration of 0.141 mg/L, the RSD (%) was calculated at 1.07%.

Table 2. Calibration accuracy for butoxybenzene.

Name	RT (min)	Area	S/N	Amount (mg/L)	Calibrated Amount (mg/L)	Accuracy (%)
Butoxybenzene	6.739	4,856.52	28.1	0.053	0.05	6.89
Butoxybenzene	6.739	8,985.51	50	0.097	0.1	−2.71
Butoxybenzene	6.739	22,939.91	110.4	0.245	0.25	−1.82
Butoxybenzene	6.739	45,799.53	331.1	0.488	0.5	−2.37
Butoxybenzene	6.740	92,623.87	677.9	0.985	1	−1.47
Butoxybenzene	6.739	944,485.47	6,425.9	10.03	10	0.3

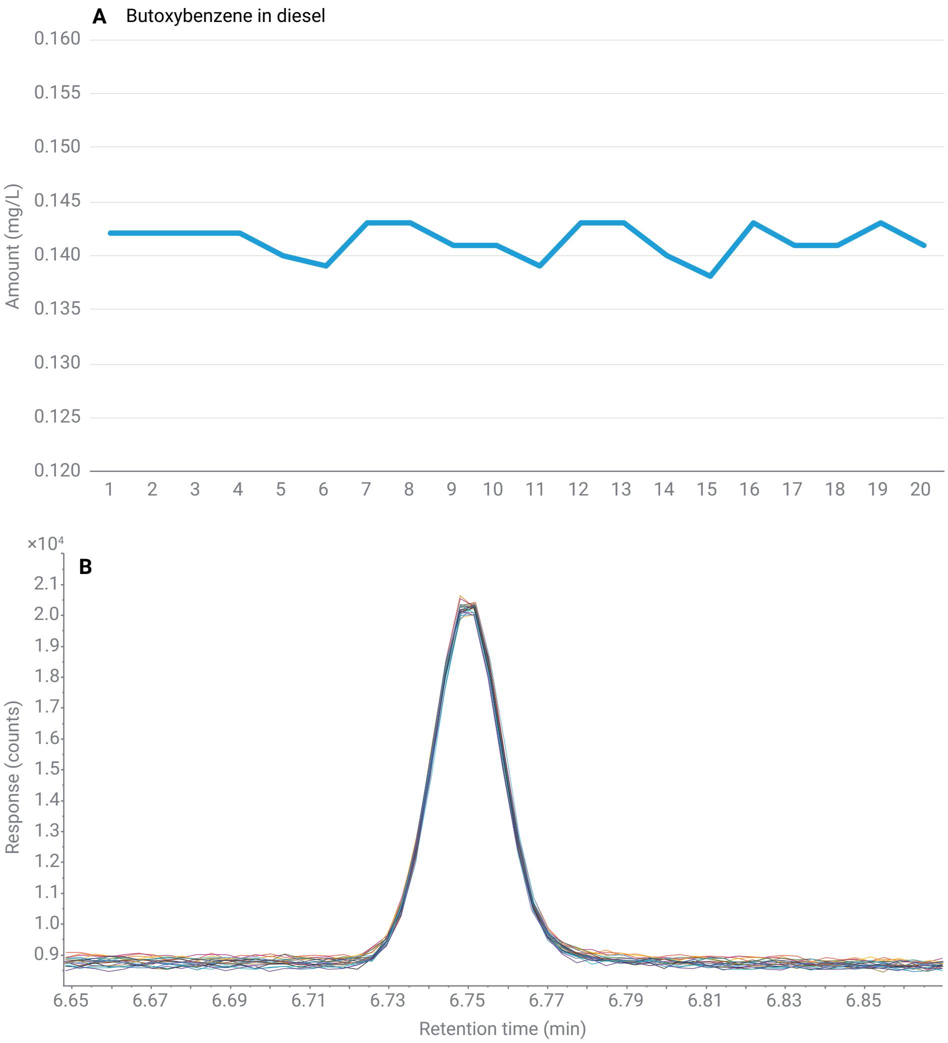


Figure 7. (A) Butoxybenzene reproducibility over 20 replicates. (B) Overlay of 20 replicates of butoxybenzene in diesel.

At the lowest calibration level of 0.05 mg/L, the peak-to-peak signal-to-noise ratio (S/N), with the noise region assigned for 0.4 minutes after the end of the peak, was 28:1 as shown in Figure 8. This indicates a method limit of detection well below the necessary measurement range.

The high precision of the Deans switch device allows for the narrowest possible heart cut from the matrix, to divert the smallest possible amount of matrix to the second column and to the MSD. As shown in Figure 9, the width of the heart cut is 0.1 minutes, and straight after the cut, the backflush can start. Figure 9 also shows the effect and clear benefit of the backflush: no matrix is visible in the FID chromatogram because all of it is flushed through the inlet split vent line.

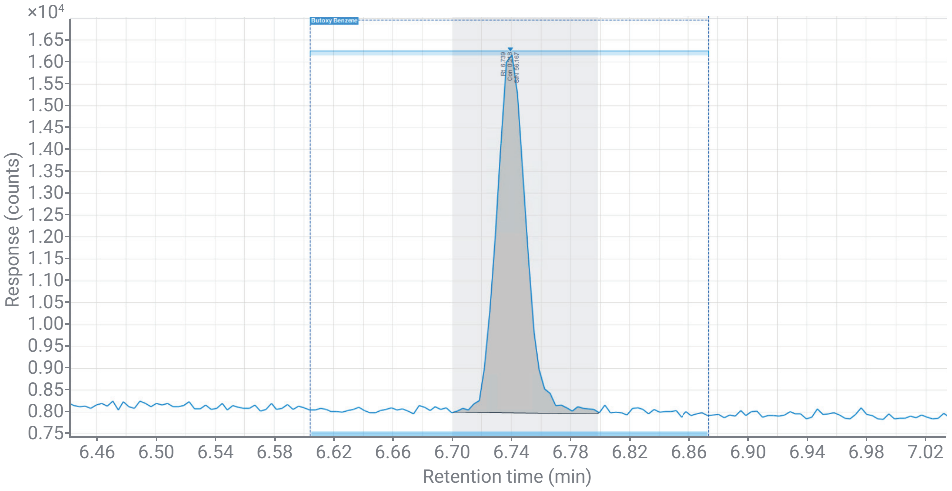


Figure 8. 0.05 mg/L butoxybenzene in xylene produces a S/N of 28:1.

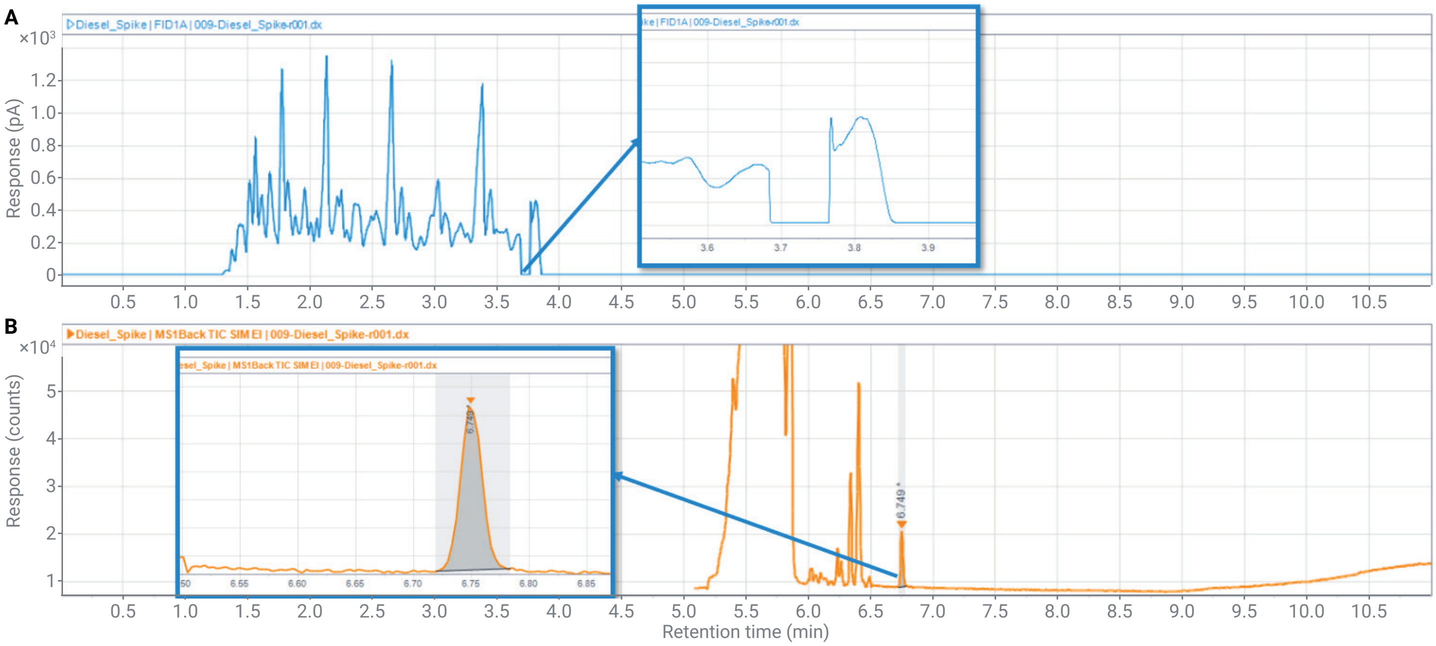


Figure 9. Heart cut window and backflush (A) of a real diesel sample spiked with butoxybenzene (B).

Conclusion

This setup allows the analysis of a newly developed fuel marker at both the specified regulatory amount (mg/L level) and when blended with unmarked fuel at low µg/L levels. The Agilent 8890 GC system equipped with a Deans switch CFT device proves to be a robust solution for the analysis of butoxybenzene marker in diesel fuel. The results obtained with the Agilent 5977 GC/MSD with extractor ion source and hydrogen as the carrier gas satisfy the sensitivity and reproducibility requirements for this analysis, and this will help laboratories that are facing helium supply shortages. With the help of a backflush system, the run time stays well below 15 minutes. In addition, the narrow heart-cut reduces the amount of sample matrix diverted to the MS detector, which helps decrease the frequency of source maintenance.

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Fast Volatile Organic Compound Analysis of Drinking Water Using the Agilent 8697 Headspace Sampler in Tandem with Intuvo 9000 GC and 5977B GC/MSD

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Abstract

This application note describes the volatile organic compound (VOC) analysis of drinking water using the Agilent 8697 headspace sampler, coupled with the Agilent Intuvo 9000 GC and Agilent 5977B GC/MSD system. The system performance in terms of repeatability, linearity, limit of quantitation, and method recovery rate was evaluated, with good results. The sample incubation time at the headspace side was optimized at 20 minutes. The separation of tested compounds under a fast oven program, using hydrogen (H_2) as the carrier gas, took approximately 6 minutes and an additional 2 minutes 30 seconds for column conditioning. With the sample overlapping capability of the headspace sampler and fast analysis on the GC side, the sample throughput can be improved for VOC analysis of drinking water.

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Introduction

VOCs are widely used in industry, agriculture, transportation, and in day-to-day household products. They can easily dissolve or leach into groundwater. The private wells located near industrial or commercial areas, gas stations, or landfills are at risk of VOC contamination. If drinking water comes from the city water supply, it is most likely treated with chlorine to kill the waterborne pathogens. The chlorine reacts with the natural organic matter, and subsequently, various VOCs form as disinfection byproducts. To ensure drinking water quality, different countries and regions have set up regulation limits on the amounts of VOCs in drinking water and developed methods to test the VOCs concentration.

To analyze the VOCs in drinking water, a headspace sampler coupled with GC/MSD is a regularly used platform.[1,2] A fixed volume of water sample is sealed and heated in a sample vial. The VOCs in the sample evaporate into the headspace of the vial. After a while, the VOC concentration between the liquid sample and the above headspace gas phase reach equilibrium. Subsequently, the VOC concentration in the headspace gas phase can be measured to determine the corresponding concentration in the liquid sample, given that the concentration in liquid is proportional to that in the gas phase. Headspace samplers provide an easy, reproducible, and clean way to extract and use the VOCs from drinking water for the following GC/MSD analysis. A GC/MSD platform usually uses a 30 to 60 m midpolar column for the VOC separation, prior to MSD identification and quantitation. The GC cycle time is typically longer than 20 minutes. The high-efficiency column, with narrower internal diameter and shorter length, can be used to accelerate the separation. With improved column resolution capability, the oven ramp can be increased accordingly to achieve fast analysis. Even if some coelution happens during the fast separation, with the aid of ion extraction capability in mass spectrometry for compound identification, an accurate qualification can still be made.

In this application note, VOCs in drinking water were analyzed using the 8697 headspace sampler, in tandem with the Intuvo 9000 GC and 5977B GC/MSD system. A high-efficiency source was used to compensate for the sensitivity loss caused by a high split ratio applied on the narrow-bore analytical column. The analysis speed was expedited by using a faster oven temperature program on the high-efficiency column. Three analytical methods were developed; one based on the MSD single ion monitoring (SIM) mode, and the other two based on the MSD scan mode. They focused on different sample concentration ranges. The VOCs tested include: halogenated hydrocarbon; benzene and its derivatives; and the gasoline additive, methyl tert-butyl ether (MTBE). The linearity, repeatability, and limit of quantitation (LOQ) for the targeted 64 VOCs were evaluated to show the system's excellent performance for VOC analysis.

Experimental

Chemicals and standards

All chemicals and standards were purchased from Anpel Laboratory Technologies (Shanghai) Inc. These included (A) a mixture of 60 VOCs in methanol at 1,000 mg/L; (B) internal calibration standards of toluene-d8, 4-bromofluorobenzene and 1,2-dichlorobenzene-d4 in methanol, at 2,000 mg/L; and (C) four single component standards in methanol, with concentrations varying from 100 to 1,000 mg/L. Analytical grade sodium chloride (NaCl), was weighed and added to the aqueous calibration solutions and real water sample, to increase VOCs partitioning to the headspace, improving sensitivity.

Working solution

The VOC standards were mixed with the single component standards and diluted by methanol to 1 and 10 mg/L working solutions, containing 64 components. The internal standard (IS) stock solution was diluted to 5 and 100 mg/L using methanol, for later use.

Calibration standards and water sample preparation

The NaCl was weighed at 2 g and added to a 20 mL headspace vial, together with 10 mL of deionized water. Aliquots of VOCs and IS working solutions were spiked into the salt solution quickly, then the vials were capped immediately and shaken to mix the standard. The calibration standards, prepared at approximately 2, 4, 10, 20, 40, 100, and 200 µg/L, with internal standards of 50 µg/L, were analyzed in scan mode. The calibration standards, ranging from 0.1 to 20 µg/L (0.1, 0.2, 0.5, 1, 2, 5, 10, and 20), with 2 µg/L IS, were analyzed in SIM mode. Replicates of middle-level and low-level calibration standards in two sets of calibrants were used for repeatability and LOQ evaluation in scan and SIM modes.

The spiked deionized water samples with calibrants and IS solutions were used for recovery tests. The recovery tests were run at three concentration levels for both SIM and scan mode-based analytical methods.

For real-sample analysis, 10 mL of tap water was added to a 20 mL sample vial containing 2 g of salt, then spiked with IS solution. The vial was capped quickly for subsequent analysis using the scan mode-based method.

Instrumentation and analytical conditions

Each prepared solution was analyzed using the 8697 headspace sampler, in tandem with the Intuvo 9000 GC and 5977B GC/MSD system. Both helium (He) and H_2 were used as the carrier gas for scan mode-based method verification. Only He was used for SIM mode-based method verification. The headspace and GC conditions are shown in Table 1.

The Agilent MassHunter acquisition software version 10.0 was used for data collection. The Agilent MassHunter qualitative analysis software version B.08.00 and MassHunter quantitative analysis software version B.08.00 were used for data analysis.

Results and discussion

For the SIM mode-based method, He was used as a carrier gas. The scan mode-based method was verified using both H_2 and He as a carrier gas. A faster oven ramp program (oven program 2, as shown in Table 1) was applied in the scan mode-based method. This is because the MSD could generate a fast enough sampling rate in the applied mass scan range (35 to 300 Da). The faster temperature program was also tested in the SIM mode-based method, however, the MSD sampling rate under SIM mode was challenged. Thus, a slower oven program (oven program 1) was used in the SIM mode-based method. The dwell time for each ion in SIM mode was optimized between 10 and 15 ms, depending on the ion number in each time segment, to achieve fast enough acquisition for accurate and repeatable quantitative analysis.

Table 1. Analytical conditions of the Agilent 8697 headspace sampler, Agilent Intuvo 9000 GC, and Agilent 5977B GC/MSD system.

Agilent Intuvo 9000 GC and 5977B GC/MSD System with High-Efficiency Ion Source	
Parameters	Setpoints
Inlet Temperature	250 °C
Liner	Agilent Ultra Inert inlet liner, split, 4 mm inner diameter (p/n 5190-2295), glass wool removed
Carrier Gas	He for SIM mode; H_2 and He for scan mode
Column Flow	Constant flow rate SIM mode-based method: 1.0 mL/min (He) Scan mode-based method: 0.7 mL/min (H_2) and 1.0 mL/min (He)
Split Ratio	100:1
Oven Program 1 (SIM Mode-Based Method)	35 °C (1.82 min), 41.18 °C/min to 200 °C, 82.37 °C/min to 230 °C (3 min)
Oven Program 2 (Scan Mode-Based Method)	35 °C (1.5 min), 50 °C/min to 200 °C, 100 °C/min to 230 °C (3.5 min)
Column	Agilent J&W DB-624 Ultra Inert Intuvo GC column module, 20 m × 0.18 mm, 1 µm (p/n 121-1324-UI-INT)
MSD Transfer Line	220 °C
MS Source	250 °C
MS Quad	150 °C
Scan Range	35 to 300 Da
Scan Speed	6,250 u/s (n = 0)
Dwell Time for Ions in SIM Method	10 to 15 ms, depending on ion number in each time segment
Gain Factor	0.5
Drawout Plate	3 mm
Agilent 8697 Headspace Sampler Parameters	
8697 Loop Size	1 mL
Vial Pressurization Gas	N_2
HS Loop Temperature	80 °C
HS Oven Temperature	80 °C
HS Transfer Line Temperature	110 °C
Vial Equilibration Time	20 min
Vial Size	20 mL, PTFE/silicone septa (p/n 8010-0413)
Vial Shaking	Level 7, 136 shakes/min with acceleration of 530 cm/S^2
Vial Fill Mode	Default
Vial Fill Pressure	15 psi
Loop Fill Mode	Custom
Loop Ramp Rate	20 psi/min
Loop Final Pressure	4 psi
Loop Equilibration Time	0.1 min
Carrier Control Mode	GC carrier control
Vent After Extraction	On

The total ion chromatograms (TICs) of 1 µg/L calibration standard (acquired in SIM mode), and 20 µg/L standard (acquired in scan mode, with H_2 and He as carrier gas, respectively) are presented in Figures 1 to 3. The separation under the faster oven program took no more than 6 minutes, with an additional 2 minutes 30 seconds for column baking. The separation run under the slower oven program took approximately 7 minutes, plus another 2 minutes 30 seconds for column cleaning.

With He as carrier gas and using oven program 1, a total of 12 compound pairs could not be resolved during the chromatography separation. When using H_2 as the carrier gas and run with oven program 2, the same 12 compound

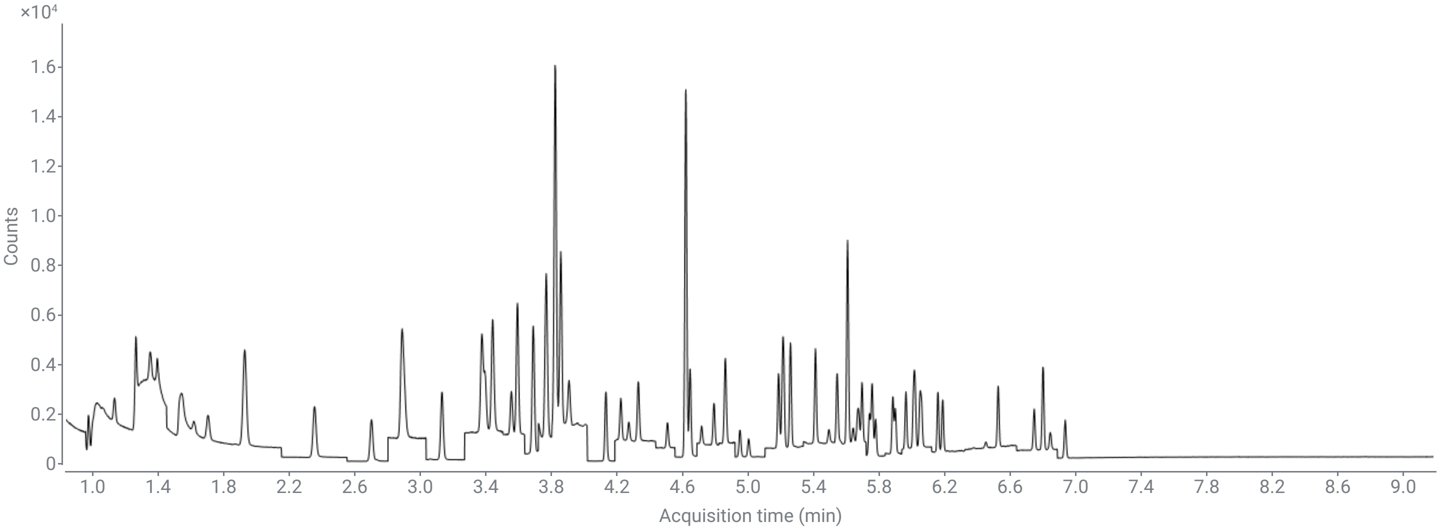

Figure 1. TIC SIM of 1 µg/L VOCs standard in 10 mL aqueous solution containing 20% (w/v) NaCl, using oven program 1 and He as carrier gas.

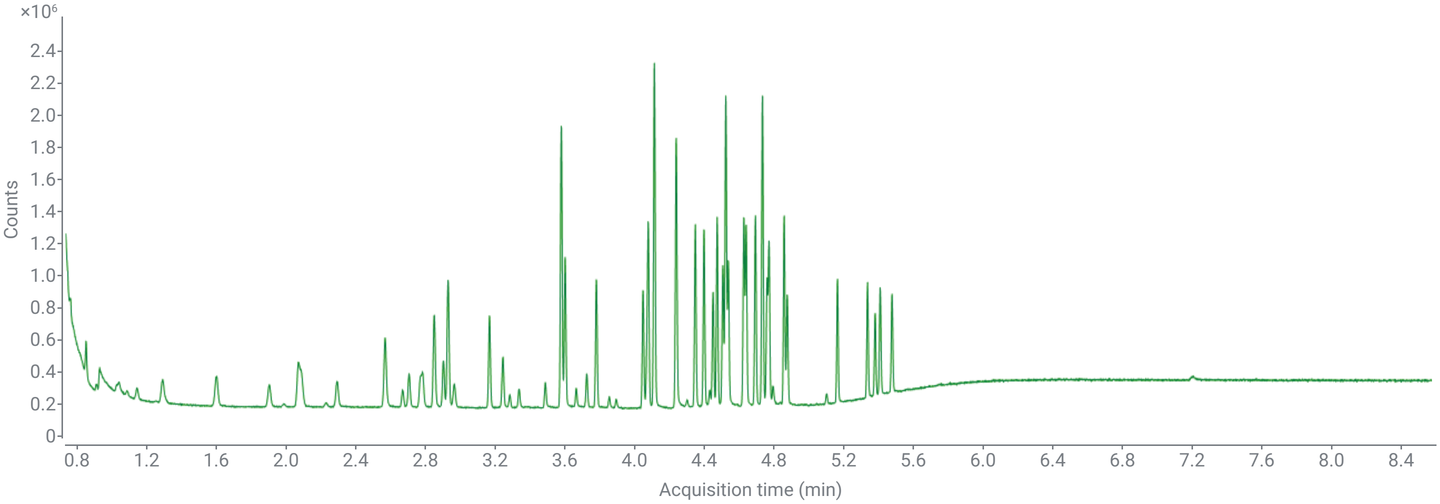

Figure 2. TIC of 20 µg/L VOCs standard in 10 mL aqueous solution containing 20% (w/v) NaCl, using oven program 2 and H_2 as carrier gas.

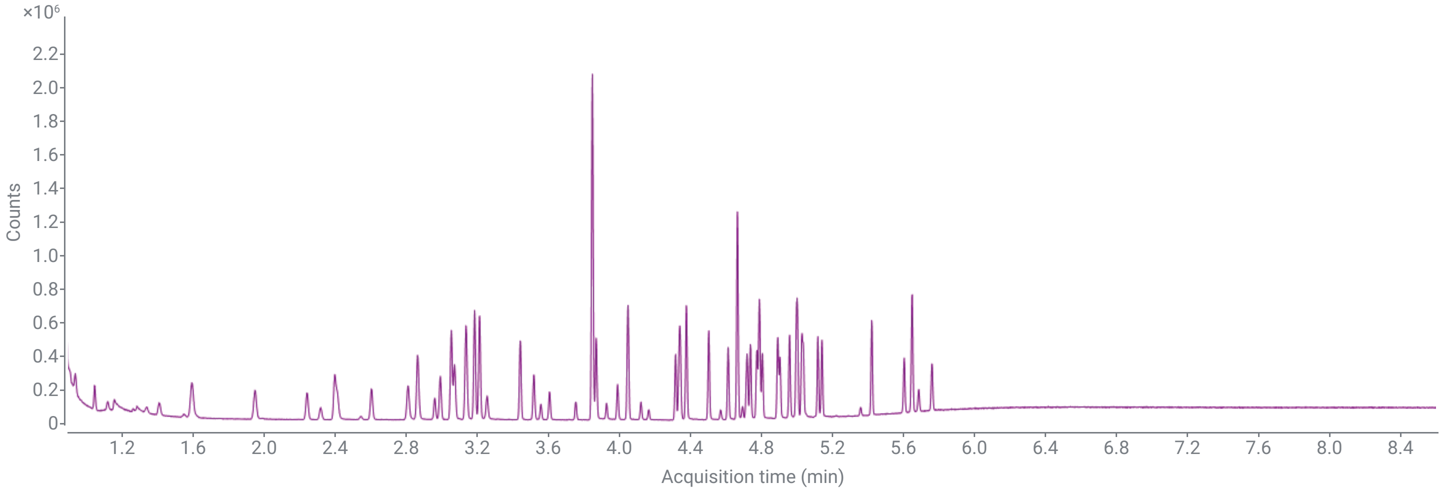

Figure 3. TIC of 20 µg/L VOCs standard in 10mL aqueous solution containing 20% (w/v) NaCl, using with oven program 2 and He as carrier gas.

pairs were also not resolved in the chromatography. These unresolved compounds could be identified and quantified based on their selected or extracted qualifier and quantifier ions at the MSD side. The additional resolving capability of MSD is one of the key reasons for fast VOC analysis on a high-efficiency column. The detailed retention time (RT) information for each compound is shown in Appendixes 1 to 3. (The coeluting compound pairs were labeled with the same number superscript in the Appendix 1 and 2)

The system repeatability in SIM and scan mode-based methods were evaluated based on the analyte absolute responses. Six replicates of 1 µg/L calibrants were analyzed in SIM mode. The response RSD% of 64 VOCs were in the range of 0.4% to 5.9% (Figure 4). The average RSD% was 1.7%, with two compounds' precision greater than 4.0%. For scan mode-based method with H_2 as carrier gas, seven replicates of 10 µg/L calibrants gave the response precision from 0.5% to 7.2%, with an average RSD% of 2.0%. Four compounds had area precision greater than 4.0%. The response precision of six 20 µg/L replicates obtained by scan mode-based method with He as carrier gas ranged from 1.0% to 5.0%, with five components showing precision greater than 4.0%. The repeatability performance demonstrated excellent sampling and detection precision.

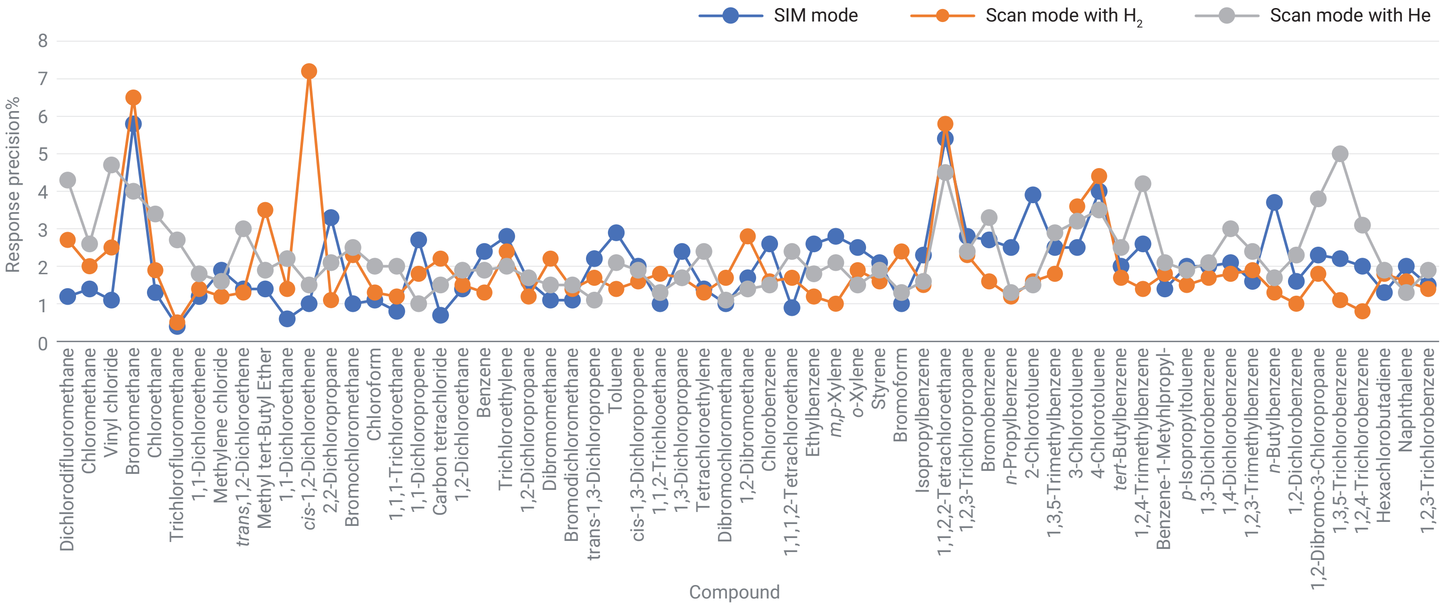

Figure 4. Area precision of calibration standards acquired in SIM and SCAN mode.

Method linearity was evaluated based on the relative response of each component to internal standard across the tested concentration range (i.e., 0.1 to 20 µg/L for the SIM mode-based method, and 2 to 200 µg/L for the scan mode-based method). Due to the different response factor of each compound, some compounds could not be detected at the lowest calibration level. The real linearity range of these compounds is noted in Appendixes 1 to 3.

All 64 VOCs acquired in SIM mode showed good linearity with the coefficients of determination R^2 greater than 0.994, and at an average of 0.998. In the scan mode-based method, when using H_2 as the carrier gas, all compounds had an R^2 greater than 0.995, and the average R^2 was 0.999. With He as the carrier gas, 21 compounds showed linearity with R^2 <0.99 in the tested concentration range. Based on the results, with the described system, it is recommended that H_2 is used as the carrier gas for the scan mode-based method, if the linearity regression is the preferred quantitation method. In the future investigation, a 6 mm drawout plate will be tested to see if the linearity performance of scan mode-based method using He as the carrier gas can be improved.

Four representative compounds eluting at the early, middle, and late part of the TIC SIM and TIC scan chromatograms are shown in Figures 5 and 6.

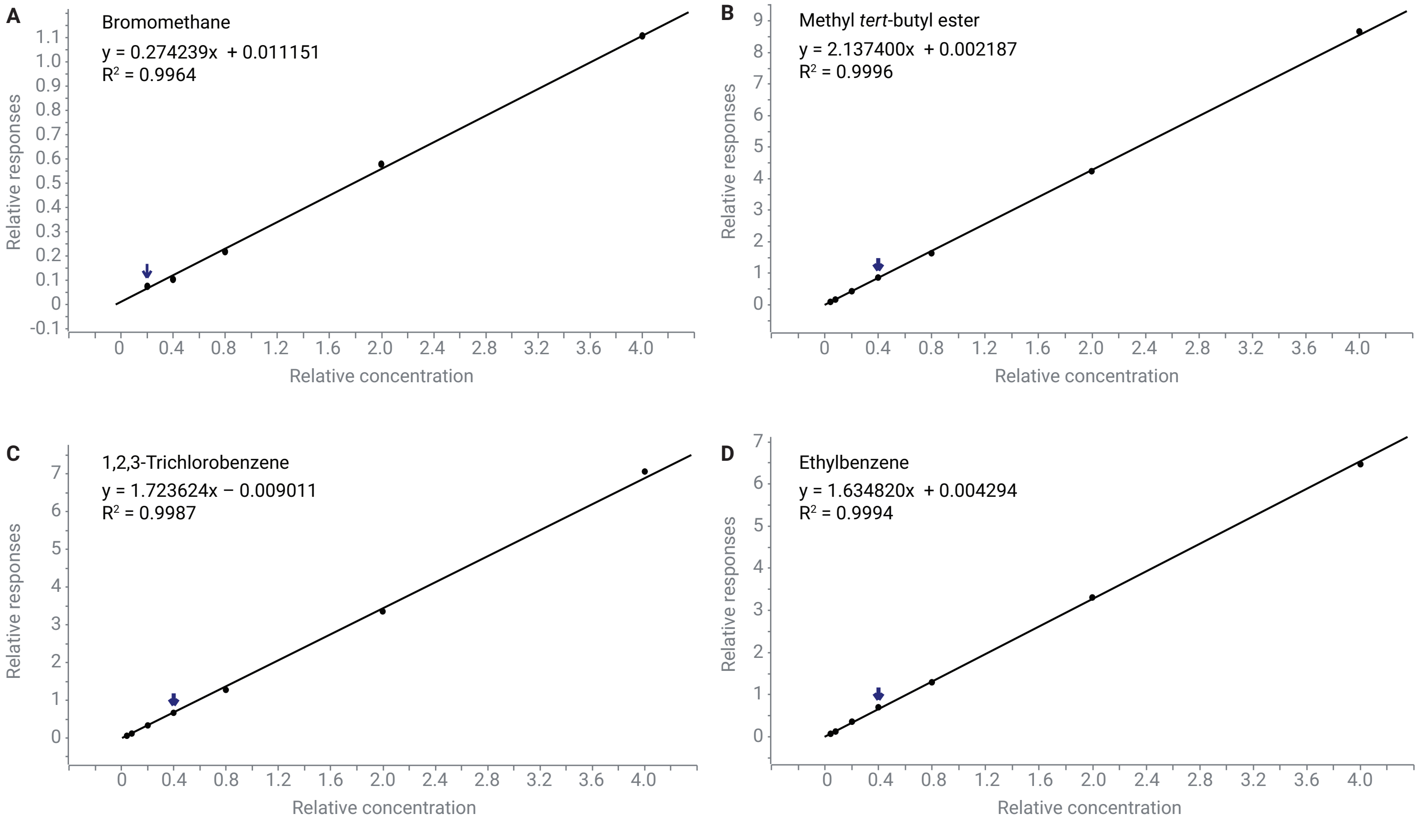

Figure 5. Calibration curves for representative compounds in scan mode using H_2 carrier gas: (A) bromomethane with R^2 0.9963; (B) methyl *tert*-butyl ether with R^2 0.9996; (C) 1,2,3-trichlorobenzene with R^2 0.9987; (D) ethylbenzene with R^2 0.9994. The concentrations ranged from 10 to 200 µg/L for bromomethane, 2 to 200 µg/L for other three compounds and the calibration curve was correlated with weight factor of 1/x.

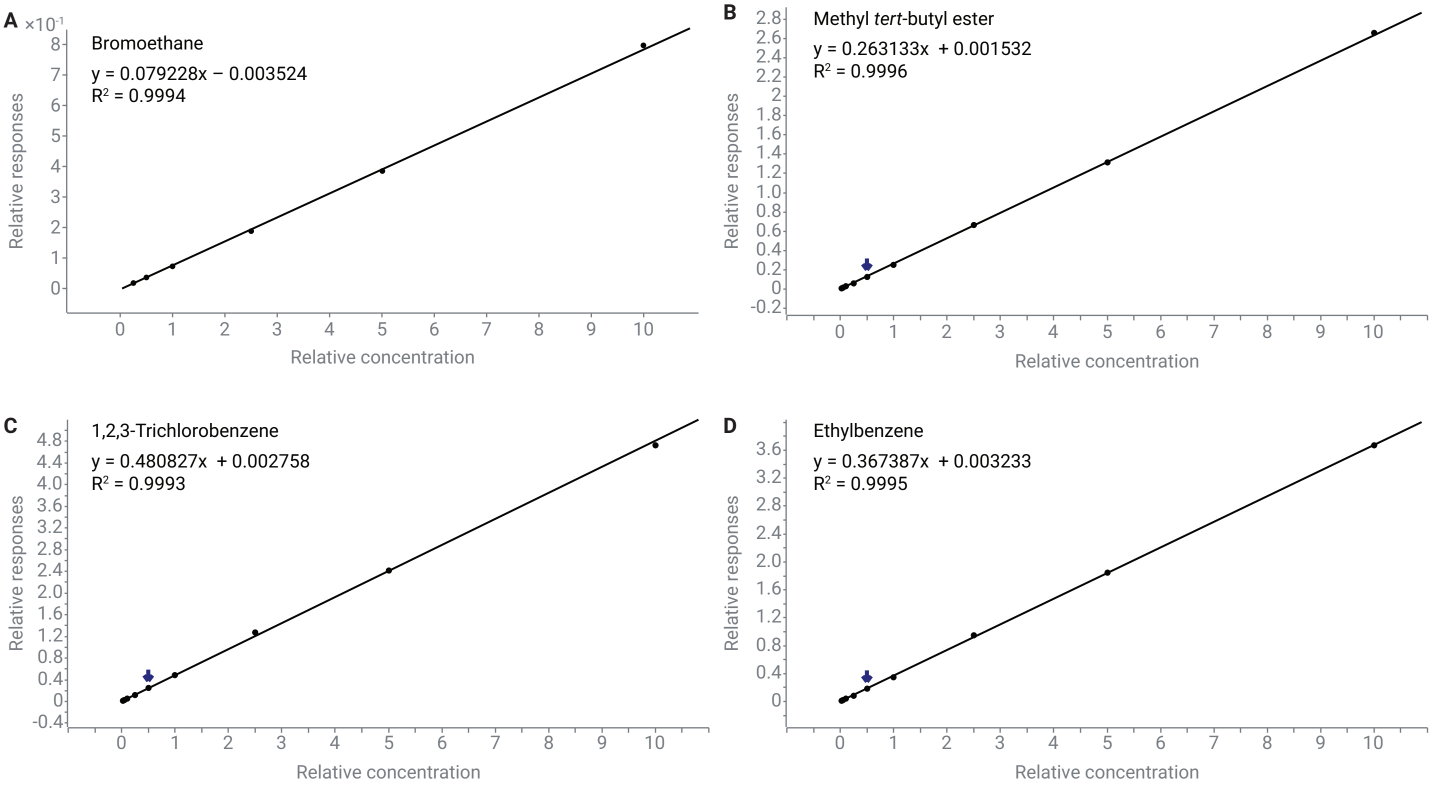

Figure 6. Calibration curves for representative compounds in SIM mode: (A) bromomethane with R^2 0.9994; (B) methyl *tert*-butyl ether with R^2 0.9995; (C) 1,2,3-trichlorobenzene with R^2 0.9993; (D) ethylbenzene with R^2 0.9994. The calibration curve was based on the concentration range of 500 ng/L to 20 µg/L for bromomethane, 100 ng/L to 20 µg/L for other three compounds and correlated with weight factor of 1/x.

The method recovery was assessed on deionized water spiked with different volumes of VOC working solution. The recovery rate in the scan mode-based method with H_2 as the carrier gas was tested at 4, 20, and 200 µg/L, with recovery performance ranging from 62 to 113% (Figure 7). The recovery performance in SIM mode was tested at three concentration levels of 100 ng/L, 1 µg/L, and 10 µg/L, and the experimental recovery ratio was from 72 to 116% (Figure 8). Bromomethane tended to show lower recovery than other components and it was the only compound with recovery below 70% in scan mode.

The LOQ for the 64 targeted VOCs were calculated based on the average signal-to-noise ratios (S/N) of seven replicates of 200 ng/L and 10 µg/L standards for SIM and scan mode-based methods, respectively. The LOQ obtained by SIM mode ranged from 0.033 to 1.51 µg/L (µg/L corresponding to µg/kg in a real water sample). The

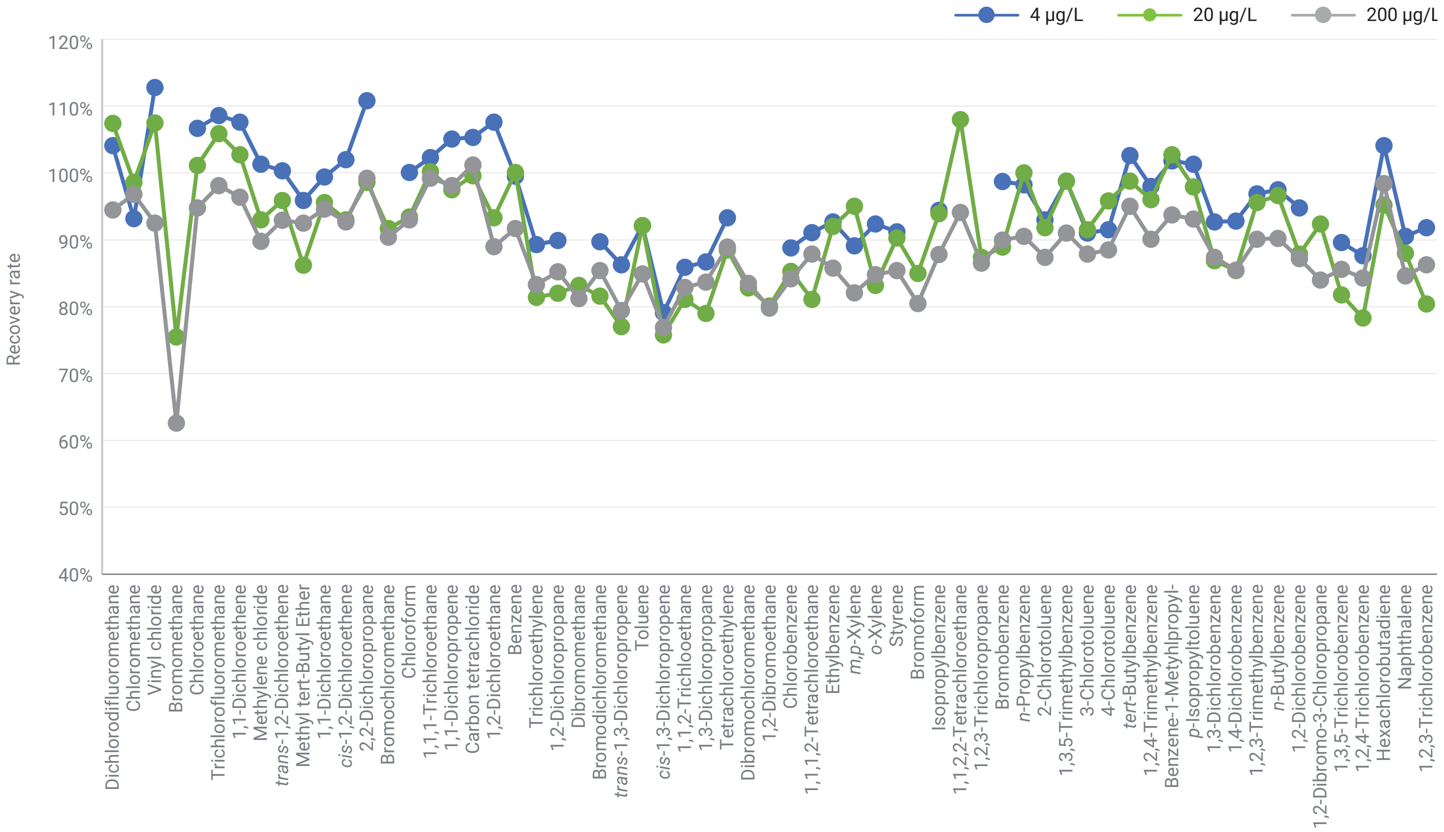

Figure 7. Recovery performance at three concentration levels: 4 (blue), 20 (green), and 200 µg/L (grey) using the scan mode-based method with H_2 as carrier gas, some compounds had no recovery results at 4 µg/L because the response at 4 µg/L was very small.

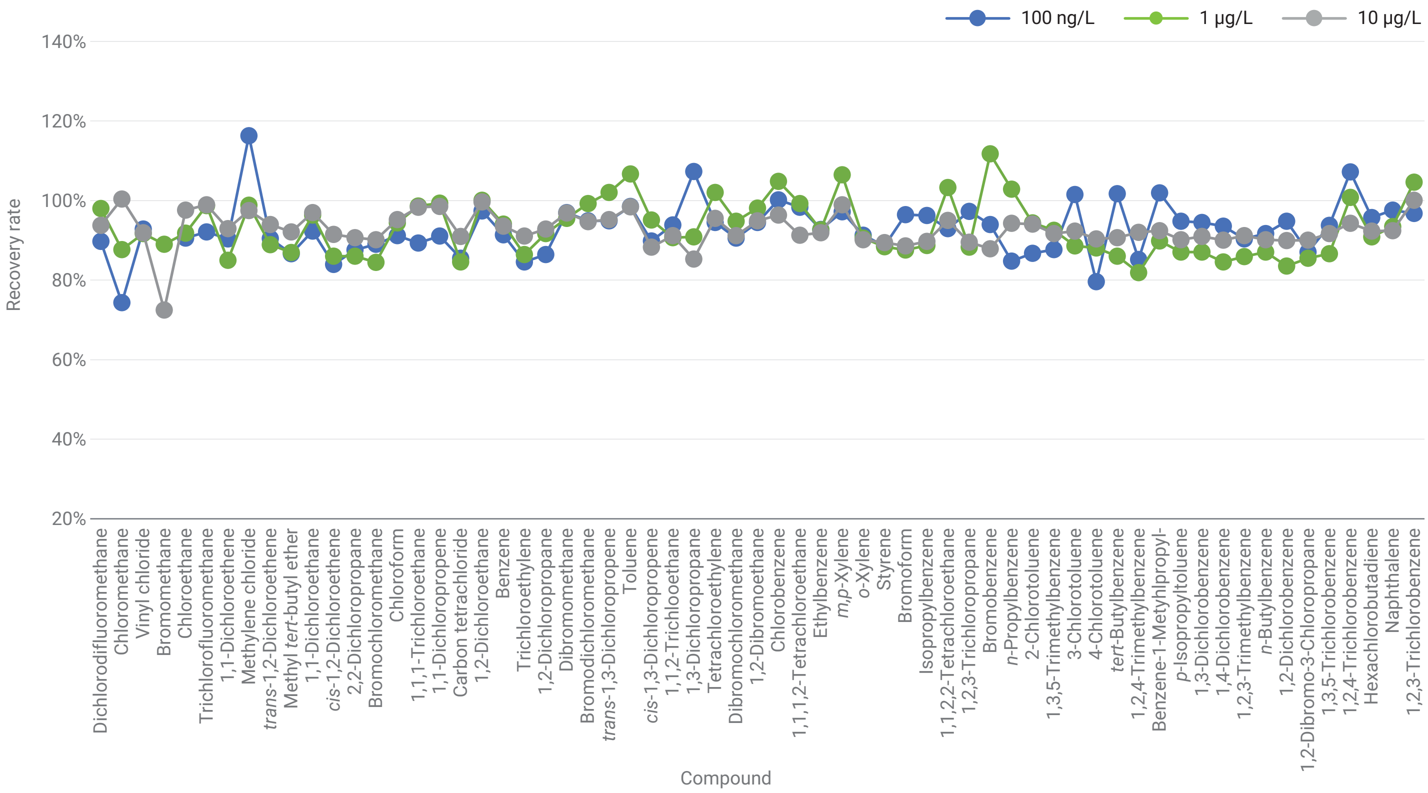

Figure 8. Recovery performance at three concentration levels: 100 ng/L (blue), 1 µg/L (green), and 10 µg/L (grey) using the SIM mode-based method. There was no recovery result for bromomethane at 100 ng/L.

LOQ obtained by scan mode with H_2 as the carrier gas was from 0.50 to 38.16 µg/L. The LOQ obtained by scan mode with He as the carrier gas ranged from 0.239 to 11.89 µg/L. The LOQs obtained with He as the carrier gas were better than those obtained with H_2 as the carrier gas. This is largely because, under the applied experimental conditions, the compound absolute response with the He carrier gas was higher and the background noise was lower, compared to that of the H_2 carrier gas. More details on the calculated LOQs are shown in Appendixes 1 to 3.

A real tap water sample was analyzed using the scan mode-based method with H_2 as carrier gas. The TIC is shown in Figure 9. The peak eluted at 2.71 minutes was chloroform, and quantitated as 8.97 µg/L. The peaks at 2.77, 2.91, 3.58 and 4.40 minutes came from IS standard. They were dibromofluromethane, 1,2-dichlorobenzene-d4, toluene-d8 and 4-bromofluorobenzene, respectively. Dibromofluromethane was not used as IS. It was included in the original IS stock solution when it was purchased. The peak at 4.80 minutes was probably octene according to a NIST library search. Since this component was not contained in the original VOC calibration standard, no further effort was made to confirm its identity. However, this unexpected compound demonstrates one of the advantages of the MSD scan mode-based VOC analysis method: the identification of unknown compounds in the real sample can be made once their concentrations are higher than the MSD detection limit.

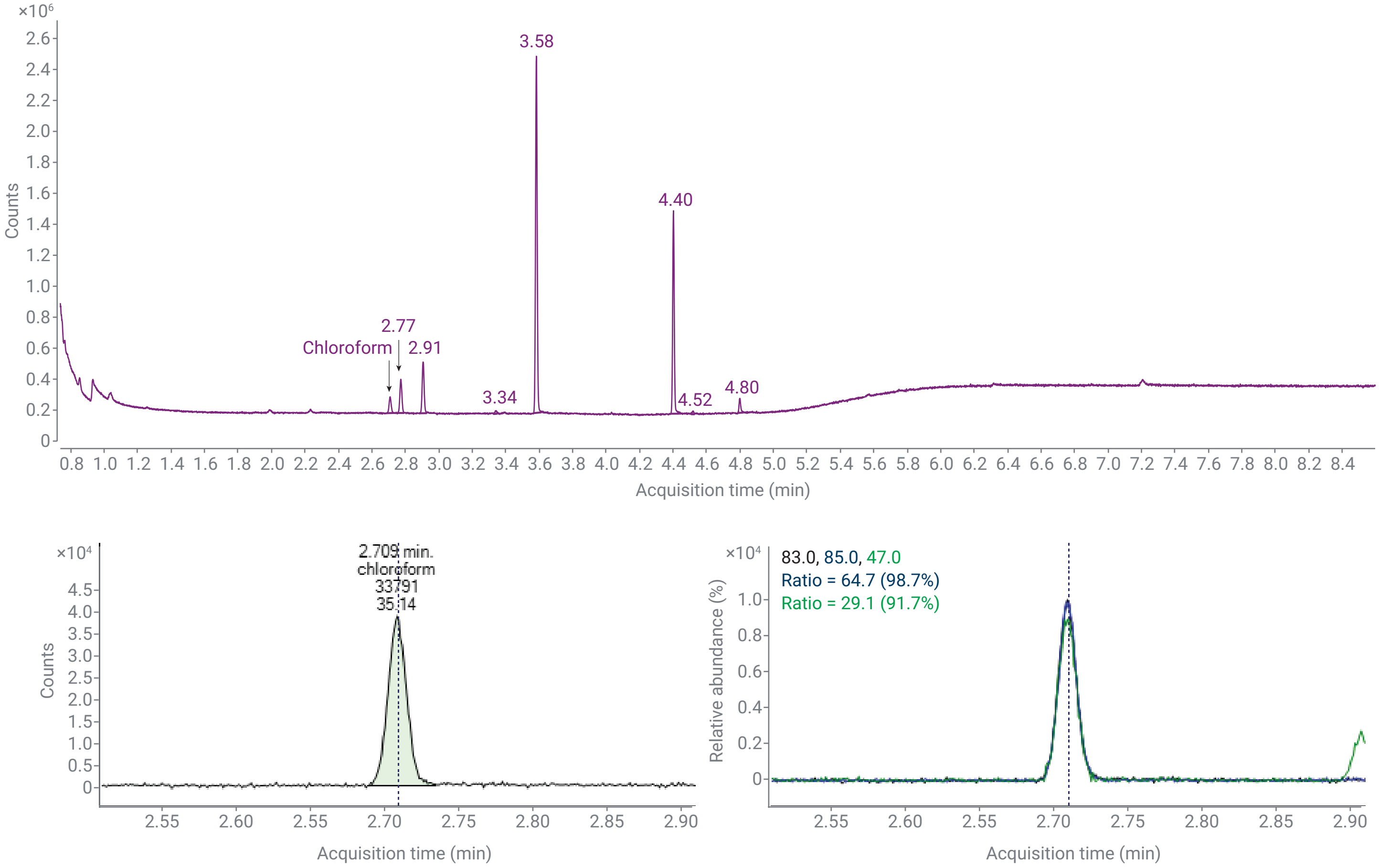

Figure 9. TIC of the tap water sample, with chloroform identified and quantified (using H_2 as the carrier gas).

Conclusion

This application note demonstrated fast VOC analysis of drinking water using the Agilent 8697 headspace sampler coupled with the Agilent Intuvo 9000 GC and 5977B GC/MSD system. The combined platform delivered good repeatability, which was demonstrated in the average response precision of 1.7% in SIM mode and 2.0% in scan mode for 64 VOCs. The linearity between 0.1 to 20 µg/L (SIM mode) and 2 to 200 µg/L (scan mode) were tested, with the average R^2 greater than 0.998. The method LOQ for SIM mode ranged from 0.033 to 1.51 µg/L, and from 0.50 to 38.16 µg/L for scan mode with H_2 as carrier gas, meeting the detection requirement for a headspace technique-based VOC analysis method. The GC cycle time for a single analysis was around 13 minutes (8.5 minutes for oven temperature program and 4 minutes for oven cooling). With such fast GC analysis and the sample overlapping capability of the Agilent 8697 headspace sampler, the lab throughput on real drinking water samples can be greatly improved.

References

1. Rothweiler, B. Analysis of Volatile Organic Compounds in Environmental Waters Using the Agilent 7697A Headspace and 7890B/5977A GC/MS, *Agilent Technologies application note*, publication number 5991-3927EN, **2014**.
2. Gautschi, P.; Prest, H. Improved Volatiles Analysis Using Static Headspace, the Agilent 5977B GC/MSD, and a High-Efficiency Source, *Agilent Technologies application note*, publication number 5991-6539EN, **2016**.

Appendix

Table A1. Instrument linearity, LOQ, precision, and method recovery rate at applied operation conditions (SIM mode-based method with He as carrier gas).

Name	RT (min)	CF R^2	Response RSD%	LOQ (µg/kg)	Recovery Rate		
					100 ng/kg	1 µg/kg	10 µg/kg
Dichlorodifluoromethane	1.13	0.9996	1.2	0.156	89.7%	98.0%	93.8%
Chloromethane	1.264	0.9971 (0.2 to 20 µg/L)	1.4	0.391	74.3%	87.7%	100.4%
Vinyl Chloride	1.352	0.9946 (0.2 to 20 µg/L)	1.1	0.328	92.8%	91.7%	91.9%
Bromomethane	1.62	0.9994 (0.5 to 20 µg/L)	5.8	1.515	NA	89.0%	72.5%
Chloroethane	1.703	0.9992	1.3	0.475	90.6%	91.8%	97.6%
Trichlorofluoromethane	1.926	0.9996	0.4	0.052	92.1%	98.7%	98.9%
1,1-Dichloroethene	2.353	0.9989	1.2	0.077	90.4%	85.0%	92.9%
Methylene Chloride	2.7	0.9992	1.9	0.044	116.3%	98.8%	97.5%
trans-1,2-Dichloroethene[1]	2.885	0.9996 (0.2 to 20 µg/L)	1.4	0.242	90.5%	88.9%	94.0%
Methyl *tert*-Butyl Ether[1]	2.901	0.9997	1.4	0.226	86.6%	86.9%	92.1%
1,1-Dichloroethane	3.13	0.9994	0.6	0.057	92.3%	96.3%	97.0%
cis-1,2-Dichloroethene[2]	3.436	0.9996 (0.2 to 20 µg/L)	1.0	0.093	84.0%	86.0%	91.5%
2,2-Dichloropropane[2]	3.44	0.9998	3.3	0.212	87.6%	86.0%	90.7%
Bromochloromethane	3.553	0.9998	1	0.247	89.0%	84.5%	90.2%
Chloroform	3.59	0.9991	1.1	0.032	91.2%	94.4%	95.2%
1,1,1-Trichloroethane	3.685	0.9995	0.8	0.059	89.3%	98.6%	98.3%
1,1-Dichloropropene[3]	3.759	0.9993	2.7	0.218	91.1%	99.4%	98.5%
Carbon Tetrachloride[3]	3.766	0.9993	0.7	0.087	85.5%	84.6%	91.0%
1,2-Dichloroethane[4]	3.852	0.9994	1.4	0.066	97.4%	100.1%	99.7%
Benzene[4]	3.855	0.9998	2.4	0.066	91.4%	94.1%	93.6%
Trichloroethylene	4.128	0.9990	2.8	0.062	84.6%	86.4%	91.1%
1,2-Dichloropropane	4.22	0.9987	1.6	0.170	86.4%	91.7%	92.8%

Name	RT (min)	CF R^2	Response RSD%	LOQ (µg/kg)	Recovery Rate		
					100 ng/kg	1 µg/kg	10 µg/kg
Dibromomethane	4.267	0.9987	1.1	0.270	97.0%	95.5%	96.9%
Bromodichloromethane	4.325	0.9969	1.1	0.056	94.9%	99.2%	94.7%
trans-1,3-Dichloropropene	4.5	0.9992 (0.2 to 20 µg/L)	2.2	0.254	94.9%	102.0%	95.2%
Toluene	4.64	0.9996	2.9	0.039	98.5%	106.7%	98.4%
cis-1,3-Dichloropropene	4.71	0.9992 (0.2 to 20 µg/L)	2	0.426	89.8%	95.1%	88.3%
1,1,2-Trichlooethane	4.786	0.9983	1	0.145	93.9%	90.7%	91.2%
1,3-Dichloropropane[5]	4.854	0.9993	2.4	0.143	107.3%	90.9%	85.3%
Tetrachloroethylene[5]	4.857	0.9993	1.4	0.045	94.5%	102.0%	95.5%
Dibromochloromethane	4.944	0.9974	1	0.121	90.6%	94.8%	91.2%
1,2-Dibromoethane	4.999	0.9991	1.7	0.216	94.5%	98.1%	94.9%
Chlorobenzene	5.18	0.9994	2.6	0.054	100.2%	104.8%	96.4%
1,1,1,2-Tetrachloroethane[6]	5.205	0.9969	0.9	0.128	98.3%	99.2%	91.3%
Ethylbenzene[6]	5.212	0.9995	2.6	0.126	92.7%	92.6%	91.9%
m,p-Xylene[7]	5.25	0.9992	2.8	0.089	97.2%	106.5%	98.9%
o-Xylene[8]	5.404	0.9992	2.5	0.181	91.3%	90.6%	90.2%
Styrene[8]	5.406	0.9993	2.1	0.131	88.6%	88.4%	89.4%
Bromoform	5.488	0.9985	1	0.184	96.5%	87.6%	88.6%
Isopropylbenzene	5.537	0.9991	2.3	0.068	96.2%	88.7%	89.7%
1,1,2,2-Tetrachloroethane	5.634	0.9988 (0.2 to 20 µg/L)	5.4	0.293	92.9%	103.3%	95.0%
1,2,3-Trichloropropane[9]	5.662	0.9987 (0.2 to 20 µg/L)	2.8	0.328	97.3%	88.3%	89.5%
Bromobenzene[9]	5.67	0.9998	2.7	0.155	94.0%	111.7%	87.9%
n-Propylbenzene	5.69	0.9996	2.5	0.121	84.8%	102.9%	94.3%
2-Chlorotoluene	5.734	0.9982	3.9	0.167	86.7%	94.4%	94.1%
1,3,5-Trimethylbenzene[10]	5.749	0.9983	2.5	0.123	87.7%	92.5%	91.7%
3-Chlorotoluene[10]	5.75	0.9985	2.5	0.195	101.5%	88.6%	92.3%
4-Chlorotoluene	5.77	0.9976	4	0.209	79.6%	88.1%	90.4%
tert-Butylbenzene	5.879	0.9987	2	0.188	101.7%	86.0%	90.7%
1,2,4-Trimethylbenzene	5.892	0.9983	2.6	0.141	85.2%	81.9%	92.0%
Benzene-1-Metyhlpropyl-	5.96	0.9977	1.4	0.087	101.9%	89.8%	92.4%
p-Isopropyltoluene[11]	6.005	0.9969	2.0	0.173	94.8%	87.0%	90.1%
1,3-Dichlorobenzene[11]	6.012	0.9975	2.0	0.069	94.5%	87.1%	91.0%
1,4-Dichlorobenzene[12]	6.044	0.9976	2.1	0.086	93.6%	84.6%	90.0%
1,2,3-Trimethylbenzene[12]	6.053	0.9975	1.6	0.153	90.4%	85.9%	91.2%
n-Butylbenzene	6.152	0.9979	3.7	0.163	91.7%	87.0%	90.1%
1,2-Dichlorobenzene	6.181	0.9980	1.6	0.080	94.8%	83.5%	89.9%
1,2-Dibromo-3-Chloropropane	6.444	0.9992 (0.5 to 20 µg/L)	2.3	0.837	87.0%	85.5%	90.0%
1,3,5-Trichlorobenzene	6.52	0.9997	2.2	0.145	93.8%	86.6%	91.7%
1,2,4-Trichlorobenzene	6.739	0.9996	2	0.214	107.2%	100.8%	94.3%
Hexachlorobutadiene	6.793	0.9991	1.3	0.069	95.7%	90.9%	92.3%
Naphthalene	6.838	0.9995	2	0.149	97.6%	93.5%	92.4%
1,2,3-Trichlorobenzene	6.93	0.9993	1.5	0.232	96.8%	104.6%	100.1%

The compound with the same superscript coeluted.

Table A2. Instrument linearity, LOQ, precision, and method recovery rate at applied operation conditions (SCAN mode-based method with H_2 as carrier gas).

Name	RT (min)	CF R^2	Response RSD%	LOQ (µg/kg)	Recovery Rate		
					4 µg/kg	20 µg/kg	200 µg/kg
Dichlorodifluoromethane	0.770	0.9999	2.7	6.63	104.1%	107.4%	94.5%
Chloromethane	0.854	0.9996	2	4.38	93.2%	98.6%	96.8%
Vinyl Chloride	0.915	0.9992	2.5	5.21	112.8%	107.5%	92.5%
Bromomethane	1.089	0.9963 (10 to 200 µg/L)	6.5	34.60	NA	75.5%	62.6%
Chloroethane	1.144	0.9992	1.9	7.97	106.7%	101.1%	94.8%
Trichlorofluoromethane	1.292	0.9998	0.5	4.22	108.6%	105.9%	98.1%
1,1-Dichloroethene	1.598	0.9995	1.4	4.82	107.6%	102.7%	96.4%
Methylene Chloride	1.908	0.9997	1.2	2.81	101.3%	93.0%	89.8%
trans-1,2-Dichloroethene[1]	2.070	0.9995	1.3	4.33	100.3%	95.9%	92.9%
Methyl *tert*-Butyl Ether[1]	2.089	0.9996	3.5	4.25	95.9%	86.2%	92.5%
1,1-Dichloroethane	2.296	0.9997	1.4	3.41	99.4%	95.6%	94.6%
cis-1,2-Dichloroethene[2]	2.570	0.9997	7.2	9.71	102.0%	93.0%	92.7%
2,2-Dichloropropane[2]	2.570	0.9988	1.1	3.37	110.8%	98.6%	99.2%
Bromochloromethane	2.671	0.9994 (10 to 200 µg/L)	2.3	20.87	NA	91.7%	90.4%
Chloroform	2.706	0.9996	1.3	3.04	100.1%	93.4%	93.0%
1,1,1-Trichloroethane	2.784	0.9988	1.2	2.60	102.3%	100.2%	99.2%
1,1-Dichloropropene[3]	2.852	0.9993	1.8	3.79	105.1%	97.5%	98.1%
Carbon Tetrachloride[3]	2.852	0.9990	2.2	10.85	105.3%	99.6%	101.2%
1,2-Dichloroethane[4]	2.933	0.9994	1.5	1.64	107.6%	93.3%	89.0%
Benzene[4]	2.931	0.9997	1.3	2.78	99.5%	100.1%	91.7%
Trichloroethylene	3.166	0.9990	2.4	2.52	89.3%	81.4%	83.3%
1,2-Dichloropropane	3.244	0.9987 (4 to 200 µg/L)	1.2	4.29	89.9%	82.0%	85.2%
Dibromomethane	3.285	0.9995 (10 to 200 µg/L)	2.2	9.16	NA	83.2%	81.2%
Bromodichloromethane	3.337	0.9995	1.4	5.06	89.7%	81.6%	85.4%
trans-1,3-Dichloropropene	3.488	0.9991	1.7	5.23	86.3%	77.0%	79.4%
Toluene	3.602	0.9992	1.4	1.39	92.1%	92.1%	84.9%
cis-1,3-Dichloropropene	3.665	0.9991 (4 to 200 µg/L)	1.6	10.18	79.1%	75.8%	76.9%
1,1,2-Trichlooethane	3.726	0.9994 (4 to 200 µg/L)	1.8	6.98	85.9%	81.1%	82.9%
1,3-Dichloropropane[5]	3.779	0.9991	1.7	2.00	86.7%	79.0%	83.7%
Tetrachloroethylene[5]	3.780	0.9992	1.3	1.43	93.3%	88.5%	88.9%
Dibromochloromethane	3.854	0.9994 (10 to 200 µg/L)	1.7	15.67	NA	82.8%	83.5%
1,2-Dibromoethane	3.893	0.9995 (10 to 200 µg/L)	2.8	8.26	NA	80.1%	79.8%
Chlorobenzene	3.049	0.9996	1.6	0.50	88.8%	85.3%	84.2%
1,1,1,2-Tetrachloroethane[6]	4.071	0.9986	1.7	6.12	91.1%	81.1%	87.9%
Ethylbenzene[6]	4.077	0.9994	1.2	1.54	92.7%	92.0%	85.8%
m,p-Xylene[7]	4.113	0.9968	1	0.91	89.1%	95.0%	82.1%
o-Xylene[8]	4.236	0.9992	1.9	1.53	92.4%	83.2%	84.8%
Styrene[8]	4.240	0.9996	1.6	1.12	91.2%	90.3%	85.4%

Name	RT (min)	CF R^2	Response RSD%	LOQ (µg/kg)	Recovery Rate		
					4 µg/kg	20 µg/kg	200 µg/kg
Bromoform	4.301	0.9997 (10 to 200 µg/L)	2.4	12.00	NA	85.0%	80.5%
Isopropylbenzene	4.347	0.9996	1.5	0.72	94.4%	93.9%	87.8%
1,1,2,2-Tetrachloroethane	4.429	0.9986 (10 to 200 µg/L)	5.8	25.56	NA	108.0%	94.1%
1,2,3-Trichloropropane[9]	4.451	0.9988 (10 to 200 µg/L)	2.3	10.0	NA	87.4%	86.5%
Bromobenzene[9]	4.451	0.9991	1.6	8.35	98.7%	88.9%	90.0%
n-Propylbenzene	4.473	0.9995	1.2	1.10	98.2%	100.0%	90.5%
2-Chlorotoluene	4.505	0.9996	1.6	2.00	93.0%	91.8%	87.4%
1,3,5-Trimethylbenzene[10]	4.522	0.9997	1.8	1.02	98.8%	98.8%	91.0%
3-Chlorotoluene[10]	4.523	0.9982	3.6	1.96	91.0%	91.5%	87.9%
4-Chlorotoluene	4.537	0.9991	4.4	1.92	91.5%	95.8%	88.5%
tert-Butylbenzene	4.627	0.9995	1.7	2.33	102.6%	98.8%	95.0%
1,2,4-Trimethylbenzene	4.639	0.9998	1.4	1.16	98.0%	96.0%	90.1%
Benzene-1-Metyhlpropyl-	4.692	0.9998	1.8	0.89	101.8%	102.7%	93.7%
p-Isopropyltoluene[11]	4.733	0.9998	1.5	0.63	101.3%	97.9%	93.1%
1,3-Dichlorobenzene[11]	4.733	0.9995	1.7	0.94	92.7%	86.9%	87.4%
1,4-Dichlorobenzene[12]	4.761	0.9994	1.8	0.81	92.8%	85.4%	85.5%
1,2,3-Trimethylbenzene[12]	4.769	0.9996	1.9	1.14	96.9%	95.6%	90.1%
n-Butylbenzene	4.858	0.9997	1.3	1.48	97.5%	96.6%	90.2%
1,2-Dichlorobenzene	4.874	0.9995	1	0.78	94.8%	87.9%	87.2%
1,2-Dibromo-3-Chloropropane	5.103	0.9990 (10 to 200 µg/L)	1.8	38.16	NA	92.4%	84.0%
1,3,5-Trichlorobenzene	5.163	0.9982	1.1	0.96	89.6%	81.8%	85.6%
1,2,4-Trichlorobenzene	5.336	0.9986	0.8	1.07	87.6%	78.3%	84.3%
Hexachlorobutadiene	5.380	0.9957	1.8	1.03	104.1%	95.2%	98.4%
Naphthalene	5.410	0.9990	1.6	0.88	90.5%	88.0%	84.6%
1,2,3-Trichlorobenzene	5.478	0.9987	1.4	1.59	91.8%	80.4%	86.3%

The compound with the same superscript coeluted.

Table A3. Instrument linearity, LOQ and precision at applied operation conditions (SCAN mode-based method with He as carrier gas).

Name	RT (min)	CF R^2	Response RSD%	LOQ (µg/kg)
Dichlorodifluoromethane	0.938	0.9991	4.3	0.733
Chloromethane	1.046	0.9996	2.6	2.332
Vinyl Chloride	1.122	0.9997	4.7	5.821
Bromomethane	1.335	0.9941 (4 to 200 µg/L)	4	11.891
Chloroethane	1.411	0.9998	3.4	4.777
Trichlorofluoromethane	1.593	0.9996	2.7	1.163
1,1-Dichloroethene	1.946	0.9958	1.8	2.092
Methylene Chloride	2.244	0.9997	1.6	3.174
trans-1,2-Dichloroethene	2.399	0.9972	3	1.860
Methyl *tert*-Butyl Ether	2.416	0.9784	1.9	1.537
1,1-Dichloroethane	2.606	0.9996	2.2	0.962
cis-1,2-Dichloroethene	2.863	0.9883	1.5	2.604
2,2-Dichloropropane	2.864	0.9969	2.1	3.231
Bromochloromethane	2.96	0.9992	2.5	5.000
Chloroform	2.991	0.9998	2	0.650
1,1,1-Trichloroethane	3.071	0.9993	2	0.616
1,1-Dichloropropene	3.136	0.9846	1	3.704
Carbon Tetrachloride	3.139	0.9995	1.5	1.392
1,2-Dichloroethane	3.213	0.9945	1.9	3.033
Benzene	3.213	0.9995	1.9	0.798
Trichloroethylene	3.442	0.9989	2	0.639
1,2-Dichloropropane	3.517	0.9986	1.7	2.000
Dibromoethane	3.559	0.9943	1.5	1.000
Bromodichloromethane	3.606	0.9934	1.5	0.517
trans-1,3-Dichloropropene	3.754	0.9984	1.1	3.535
Toluene	3.87	0.9959	2.1	0.558
cis-1,3-Dichloropropene	3.928	0.9985	1.9	4.697
1,1,2-Trichloroethane	3.987	0.9935	1.3	5.642
1,3-Dichloropropane	4.044	0.9987	1.7	2.709
Tetrachloroethylene	4.048	0.9980	2.4	0.239
Dibromochloromethane	4.125	0.9946	1.1	1.457
1,2-Dibromoethane	4.166	0.9966	1.4	2.857
Chlorobenzene	4.317	0.9974	1.5	0.391
1,1,1,2-Tetrachloroethane	4.334	0.9958	2.4	0.460
Ethylbenzene	4.342	0.9699	1.8	1.258
m,p-Xylene	4.377	0.9624	2.1	0.792
o-ylene	4.502	0.9671	1.5	3.370
Styrene	4.503	0.9646	1.9	1.787
Bromoform	4.612	0.9944	1.3	4.138
Isopropylbenzene	4.683	0.9682	1.6	1.284
1,1,2,2-Tetrachloroethane	4.694	0.9526	4.5	4.434
1,2,3-Trichloropropane	4.713	0.9773	2.4	2.546
Bromobenzene	4.72	0.9981	3.3	1.602
n-Propylbenzene	4.736	0.9872	1.3	1.093
2-Chlorotoluene	4.775	0.9945	1.5	2.078
1,3,5-Trimethylbenzene	4.784	0.9760	2.9	1.683
3-Chlorotoluene	4.79	0.9925	3.2	1.749
4-Chlorotoluene	4.804	0.9951	3.5	2.058
tert-Butylbenzene	4.892	0.9873	2.5	3.213
1,2,4-Trimethylbenzene	4.904	0.9739	4.2	1.673
Benzene-1-Metyhlpropyl-	4.959	0.9888	2.1	1.204
p-Isopropyltoluene	4.995	0.9803	1.9	1.491
1,3-Dichlorobenzene	5.001	0.9959	2.1	0.784
1,4-Dichlorobenzene	5.027	0.9988	3	0.887
1,2,3-Trimethylbenzene	5.035	0.9844	2.4	1.336
n-Butylbenzene	5.117	0.9890	1.7	1.725
1,2-Dichlorobenzene	5.139	0.9980	2.3	0.927
1,2-Dibromo-3-Chloropropane	5.36	0.9896 (5 to 200 µg/L)	3.8	5.731
1,3,5-Trichlorobenzene	5.421	0.9959	5	0.345
1,2,4-Trichlorobenzene	5.603	0.9968	3.1	0.623
Hexachlorobutadiene	5.647	0.9806	1.9	0.462
Naphthalene	5.683	0.9871	1.3	2.180
1,2,3-Trichlorobenzene	5.758	0.9968	1.9	1.414

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Application Note

Environmental

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 (H_2) 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 H_2 carrier gas.

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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 (H_2) 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 H_2-related issues and helps improve performance with H_2 carrier gas in GC/MS. The HydroInert source with H_2 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 HydroInert source to allow the use of H_2 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 H_2 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	*m*-Nitroaniline	98	Pyrene
15	1,4-Dichlorobenzene	57	Acenaphthene	99	Aramite
16	Benzyl alcohol	58	2,4-Dinitrophenol	100	*p*-Terphenyl-d$_{14}$ (surrogate)
17	1,2-Dichlorobenzene	59	4-Nitrophenol	101	Aramite II
18	2-Methylphenol (o-cresol)	60	Pentachlorobenzene	102	*p*-(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	*p*-Cresol	63	1-Naphthalenamine	105	Benzyl butyl phthalate
22	N-Nitrosodi-*n*-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	*o*-Toluidine	67	Thionazin	109	Bis(2-ethylhexyl) phthalate
26	Hexachloroethane	68	Fluorene	110	Di-*n*-octyl phthalate
27	Nitrobenzene-d$_5$ (surrogate)	69	4-Chlorophenyl phenyl ether	111	7,12-Dimethylbenz[a]anthracene
28	Nitrobenzene	70	5-Nitro-*o*-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-cd)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	a,a-Dimethylphenethylamine	80	Phenacetin	122	Acenaphthalene-d$_{10}$ (internal standard)
39	*p*-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 µL, PTFE-tip plunger (part number G4513-80203)
Column	Agilent DB-5ms Ultra Inert, 20 m × 0.18 mm, 0.36 µm (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 µL
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 *m/z*
Tune	etune.u
Gain Factor	0.5
Threshold	0
A/D Samples	4

Method development

Switching carrier gas from He to H_2 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 µg/mL for most compounds. For example, if the typical EPA method 8270 analysis with He carrier gas used a 30 m × 0.25 mm, 0.25 µm DB-5ms Ultra Inert column was changed to use a 20 m × 0.18 mm, 0.18 µm DB-5ms Ultra Inert column for H_2 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 µg/mL injected concentration (25 ng/mL on column); using etune.u did not solve the issue. Another investigated method used the 30 m × 0.25 mm, 0.25 µm DB-5ms Ultra Inert column with a pulsed splitless injection and 1.5 mL/min flow rate. This method could reach the 0.1 µg/mL lower-end concentration for most compounds but had issue with severely fronting peaks above ~75 µg/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 µg/mL. For the column referenced in this work (20 m × 0.18 mm, 0.36 µm 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 µg/mL range. While atune would be preferred, the lowest concentration tended to end at 0.2 µg/mL for most of the compounds.

Results and discussion

Mass spectral fidelity

A major concern with H_2 carrier gas is changes in the mass spectra of nitro compounds and heavily halogenated compounds. In the presence of H_2, 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 HydroInert source with nitrobenzene. In an experiment with an extractor source with a 3 mm extraction lens, H_2 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 H_2 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 HydroInert 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 HydroInert source retention of nitrobenzene), where there is an improved 123/93 ratio using the HydroInert source, while the extractor source EIC overlay shows significant conversion to 93 *m/z* and significant tailing.

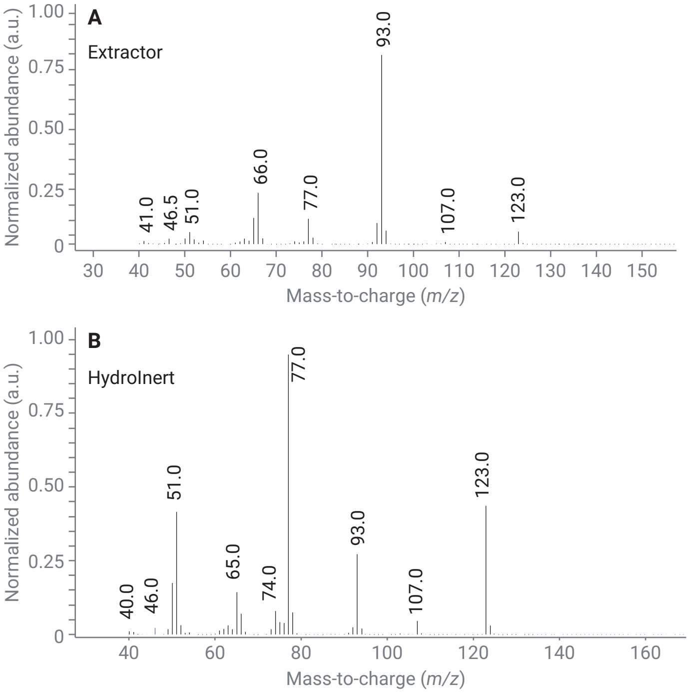

Figure 1. Mass spectra for peak eluting at nitrobenzene retention time with H_2 carrier gas in (A) extractor source with 3 mm extraction lens showing hydrogenation to aniline with the abundant 93 *m/z* ion and (B) Agilent HydroInert source, showing an improved mass spectrum that correlates to nitrobenzene.

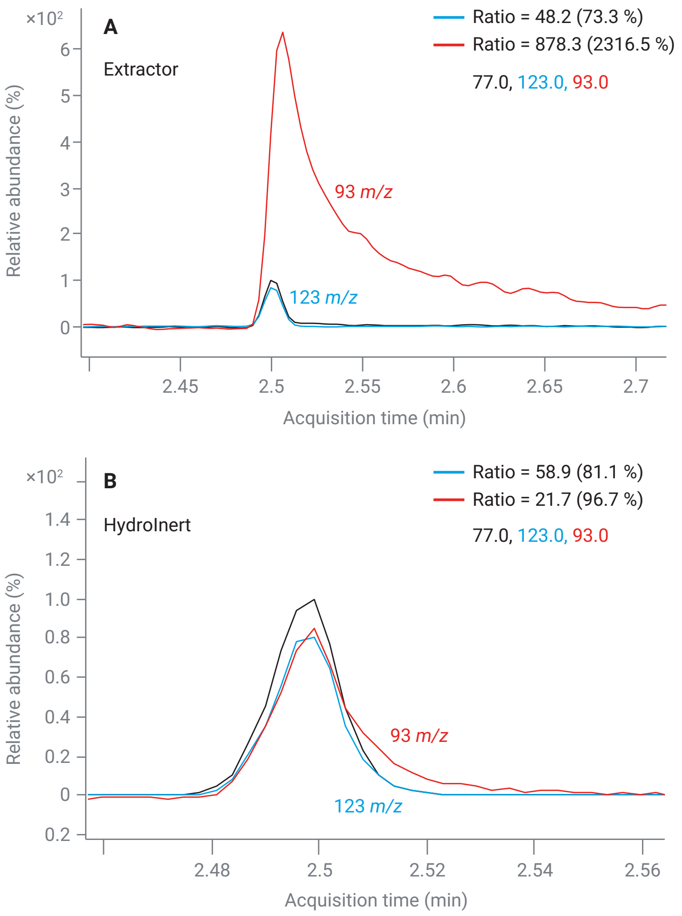

Figure 2. EICs of nitrobenzene with H_2 carrier gas in (A) extractor source with 3 mm extraction lens showing hydrogenation to aniline with the abundant 93 *m/z* ion and (B) Agilent HydroInert source, showing an improved 123 versus 93 *m/z* ratio.

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 H_2 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 H_2 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.

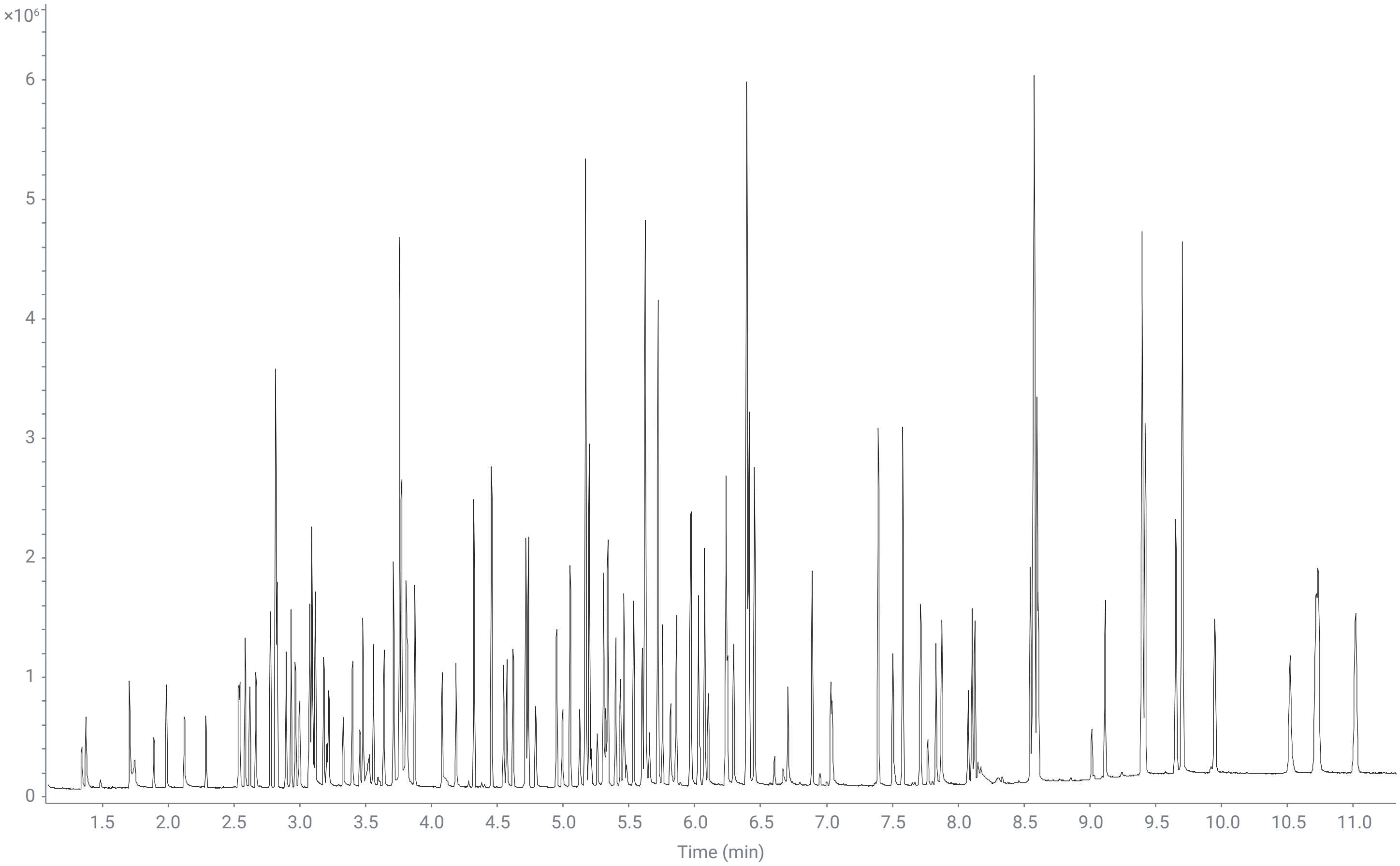

Figure 3. TIC of the 20 µg/mL calibration standard containing 119 target analytes and surrogates and six internal standards using H_2 carrier gas and the Agilent HydroInert source.

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.

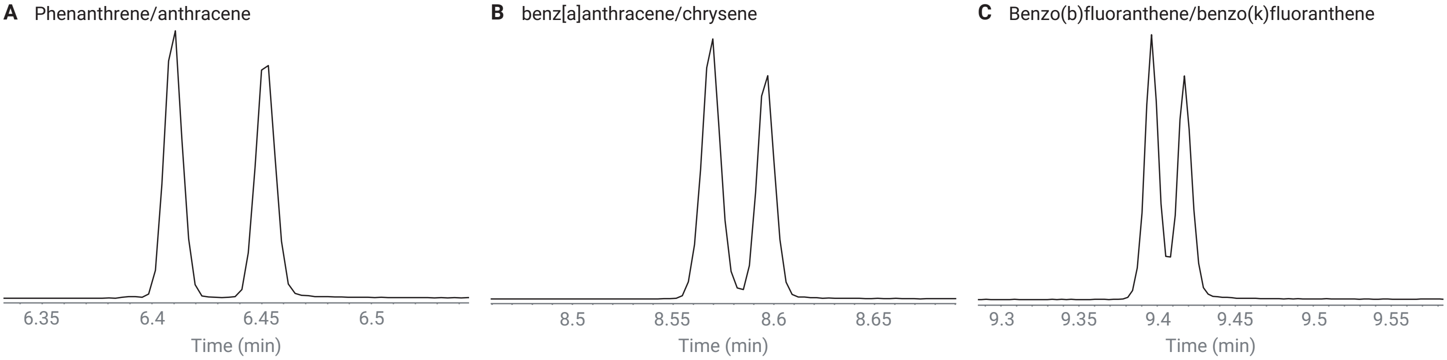

Figure 4. Midlevel standard (5 µg/mL) EICs for critical isomer pairs: (A) phenanthrene and anthracene (EIC 178 *m/z*); (B) benz[a]anthracene and chrysene (EIC 228 *m/z*); (C) benzo(b)fluoranthene and benzo(k)fluoranthene (EIC 252 *m/z*).

Response factor comparison between hydrogen and helium carrier gases

When moving an analysis from He to H_2 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 H_2 carrier gas. Since the H_2 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 H_2 HydroInert results. For the H_2 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 H_2 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 H_2 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 gas[3], GC/MS single quadrupole analysis with He and pulsed split injection[4], and GC/MS single quadrupole analysis with the Agilent HydroInert source and H_2 carrier gas.

	Response Factors			
Compound	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-*n*-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-*n*-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 HydroInert 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 R^2 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 H_2 carrier gas and the HydroInert 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 H_2 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 H_2 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 HydroInert source and H_2 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 HydroInert source with H_2 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 H_2 and the HydroInert source, while helium-collected data required a linear fit for the same calibration range. Pentachlorophenol also had matched calibration ranges between the He and H_2 results of 0.5 to 100 µg/mL, but the H_2 data required a linear fit. On the positive side, some compounds had wider calibration ranges with H_2 and the HydroInert 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 H_2 carrier gas with the HydroInert 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 H_2 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	
Propyzamide	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	
p-Terphenyl-d_{14}	7.716	0.422	14.16				
Aramite II	7.770	0.044	12.41			0.2	
p-(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-*n*-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 H_2 carrier gas with the HydroInert source (Figure 5B). The average RF %RSDs are remarkably similar between the results for He carrier gas and H_2 carrier gas with the HydroInert source, at 6.33% RSD for He carrier gas, and 6.59% RSD for H_2 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 H_2 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*.

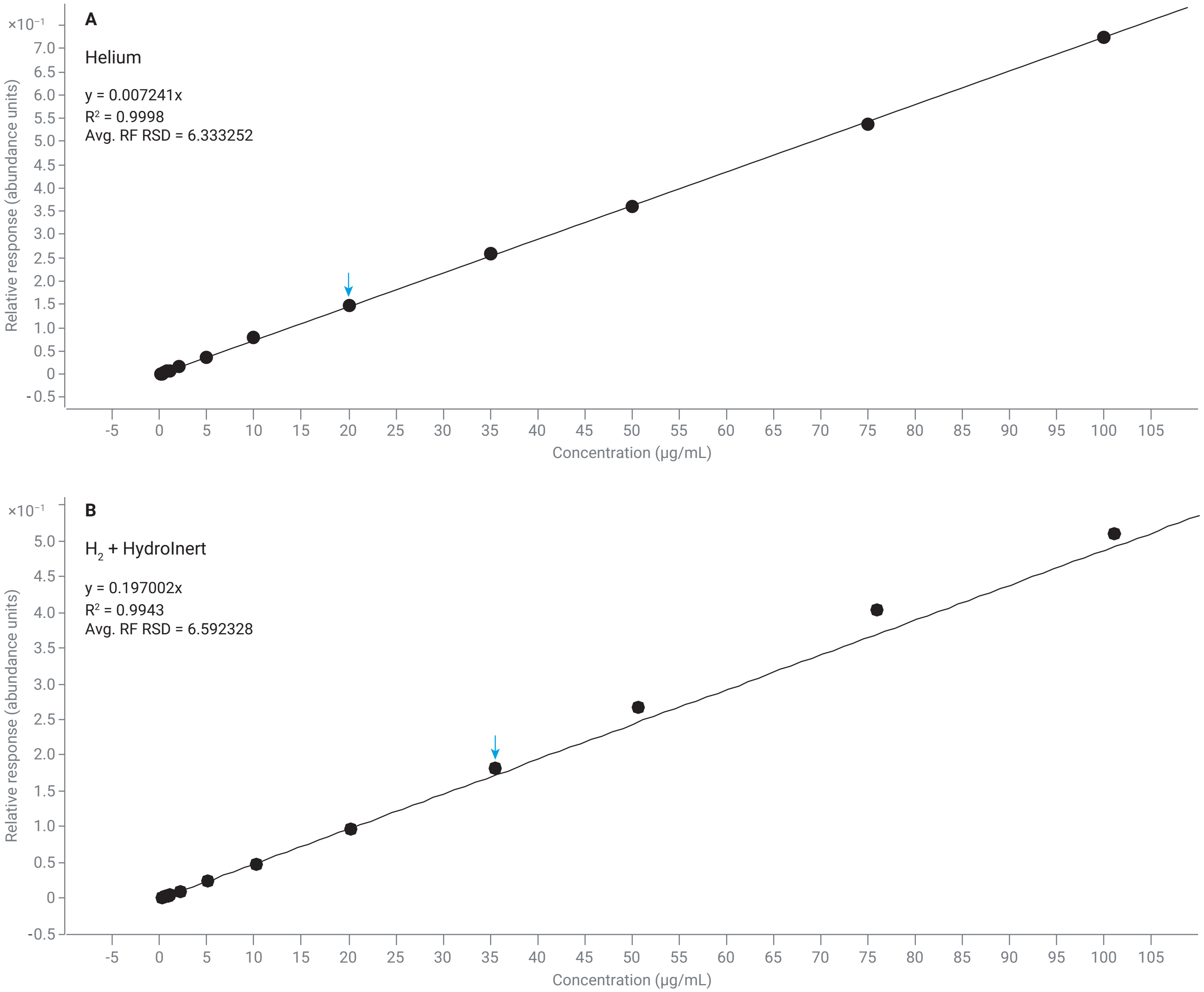

Figure 5. Nitrobenzene linear range (0.1 to 100 µg/mL) collected on a GC/MS system in (A) He and in (B) H_2 carrier gas with the Agilent HydroInert source.

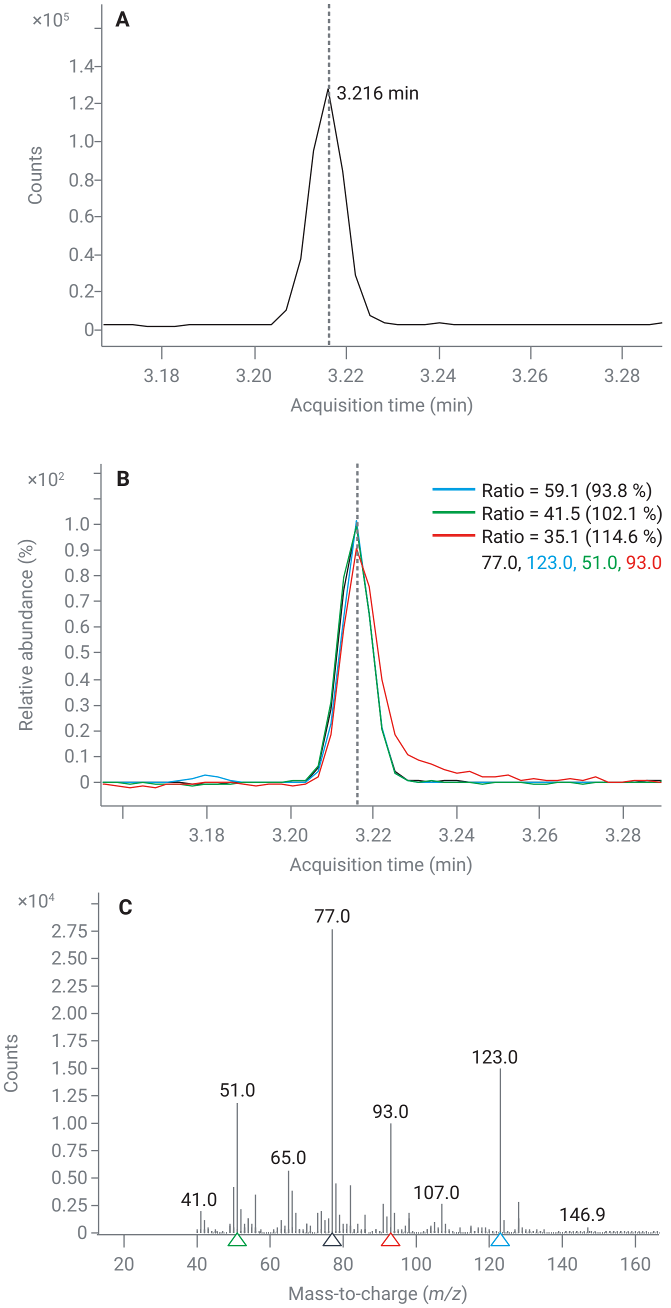

Figure 6. Nitrobenzene compound information for the 10 µg/mL standard; (A) extracted ion chromatogram (EIC 77 *m/z*) of the base peak; (B) overlay of base peak (77 *m/z*) and top three qualifier EICs (123, 51, 93 *m/z*); (C) raw mass spectrum for nitrobenzene peak at 3.216 minutes.

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 HydroInert source in GC/MS with H_2 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 concetrations: 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 (*o*-cresol)	15.6	1.43%
Bis(2-chloro-1-methylethyl) ether	14.4	1.91%
1-Nitrosopyrrolidine	14.9	2.73%
p-Cresol	14.2	1.08%
N-Nitrosodi-*n*-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%
o-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%
a,a-Dimethylphenethylamine	14.0	2.25%
4-Chloroaniline	15.5	1.80%
2,6-Dichlorophenol	17.9	1.34%
Hexachlorobutadiene	13.5	3.66%
N-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%
m-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-*o*-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%
p-Terphenyl-d$_{14}$	15.3	1.98%
p-(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[a]anthracene	13.7	0.98%
Chrysene	14.5	1.31%
Bis(2-ethylhexyl) phthalate	15.2	1.89%
Di-*n*-octyl phthalate	14.3	1.30%
7,12-Dimethylbenz[a]anthracene	12.2	1.40%
Benzo[b]fluoranthene	14.7	1.50%
Benzo[k]fluoranthene	15.4	2.94%
Benzo[a]pyrene	15.4	2.07%
3-Methylcholanthrene	14.6	2.77%
Dibenz[a,j]acridine	13.0	1.58%
Indeno(1,2,3-cd)pyrene	15.8	1.44%
Dibenz[a,h]anthracene	15.5	2.18%
Benzo[ghi]perylene	15.5	1.56%

Conclusion

A method for testing SVOCs using H_2 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 H_2 carrier gas with GC/MS systems, especially for environmental analyses, such as EPA method 8270.

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Application Note

Environmental

Analysis of PAHs Using GC/MS with Hydrogen Carrier Gas and the Agilent HydroInert Source

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Abstract

The Agilent 8890 GC and the Agilent 5977C GC/MSD were used with hydrogen carrier gas and a new source optimized for hydrogen operation. The Agilent HydroInert source, when used with the method described in this application note, provides excellent peak shape, sensitivity, and linearity across a calibration range of 0.25 to 1,000 pg for the analysis of polycyclic aromatic hydrocarbons (PAHs). By proper selection of instrument configuration and operating conditions, the system with hydrogen carrier gas can generate results comparable to or better than those with helium. System precision and robustness are demonstrated with replicate injections of an extract from a high organic content soil.

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Introduction

PAHs are a group of chemical compounds that are composed of at least two or more fused conjugated benzene rings with a pair of carbon atoms shared between rings in their molecules. Because PAHs originate from multiple sources, they are widely distributed as contaminants throughout the world. Given their ubiquitous nature, they are monitored as trace contaminants in many different food products ranging from seafood to edible oils to smoked meats. They are also monitored in the environment in air, water, and soil. PAHs have been analyzed by multiple techniques including HPLC/UV, GC/FID, GC/MS, and GC/MS/MS.

This application note focuses on GC/MS in selected ion monitoring (SIM) mode using hydrogen as the GC carrier gas. While helium is generally considered the best carrier gas for GC/MS analysis, its reoccurring shortages have increased demand for applications using hydrogen as the carrier gas. When adopting hydrogen for GC/MS analysis, there are several things to consider.

First, hydrogen is a reactive gas, and may potentially cause chemical reactions in the inlet, column, and sometimes the mass spectrometer electron ionization (EI) source that can change analysis results. It is important to ensure that there are no chemical reaction problems between analytes and hydrogen gas at elevated temperatures in the GC/MS.

Second, it is essential to use a reliable source of clean hydrogen gas. For long-term use, generators with a >99.9999% specification and low individual specs on water and oxygen are recommended. Moisture filters are recommended for use with hydrogen generators. For short-term use, cylinders with chromatographic or research-grade hydrogen are acceptable. It is also recommended that anyone working with flammable or explosive gases take a lab safety course covering proper gas handling and use.

Additionally, for GC/MS applications, hardware changes in the gas chromatograph and mass spectrometer may be required when switching to hydrogen carrier gas. The Agilent EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion user guide[1] describes in detail the steps for conversion. These steps include selection of the inlet liner, column, vacuum pump, and EI source. Chromatographic conditions and injection solvent may also need to be adjusted.

One of the advantages observed with hydrogen carrier gas is a reduced need for EI source cleaning. A similar improvement is observed when using Agilent JetClean technology, which uses a low continuous flow of hydrogen into the source during the analysis.[2,3,4] A second advantage often observed with hydrogen carrier gas is the ability to decrease the analysis time while maintaining chromatographic resolution.

PAHs are relatively durable compounds and therefore can be analyzed with hydrogen carrier gas when using the optimized method and following the recommendations described in this application note. Other challenges with PAH analysis addressed in this work include peak tailing, often seen for late-eluting analytes, and ISTD response inconsistency across the calibration range. With the optimized method using the HydroInert source, excellent linearity of $R^2 \geq 0.999$ was observed for all 27 analytes over their respective calibration ranges. Of the 27 analytes, 18 had a calibration range from 0.1 to 1,000 pg, eight from 0.25 to 1,000 pg, and one from 0.5 to 1,000 pg. Method detection limits (MDL) ranged from 0.03 to 0.20 pg, with an average of 0.09 pg.

Experimental

The system used in this experiment was configured to minimize the potential problems with hydrogen carrier gas in PAH analysis. The important parameters used were:

- **Hydrogen gas:** In-house hydrogen with 99.9999% purity specification and low individual specs on water and oxygen was used as a carrier gas.
- **Pulsed splitless injection:** Used to maximize transfer of the PAHs, especially the heavy ones, into the column.
- **Column dimensions:** An Agilent J&W DB-EUPAH, 20 m × 0.18 mm id, 0.14 µm (part number 121-9627) was used to maintain optimal gas flow and inlet pressure.
- **Inlet liner:** The Agilent universal Ultra Inert mid-frit liner (part number 5190-5105) was found to give good peak shape, inertness, and longevity with the soil extracts.
- **HydroInert EI source:** PAHs present unique challenges with respect to the MS EI source, even with helium as the carrier gas.[2] With hydrogen carrier gas, the performance of PAHs is generally improved, especially with the HydroInert source, which is optimized for use with hydrogen. The 9 mm extractor lens is the default included with the HydroInert source and the best choice for PAH analysis, as it provides the best calibration linearity, precision of response, and peak shape.

Figure 1 shows the system configuration used in this study.

The instrument operating parameters are listed in Tables 1 and 2. Instrument temperatures must be kept high enough to prevent deposition of the highest boiling PAHs. The inlet and MSD transfer line are maintained at 320 °C. The MS source is operated at 320 °C.

Pulsed splitless injections are used to maximize transfer of the PAHs, especially the heavy ones, into the column. The Ultra Inert mid-frit liner works well for this application. The frit transfers heat to the PAHs and blocks the line of sight to the inlet base. If the PAHs condense on the inlet base, they are difficult to vaporize and sweep back into the column.

PAH calibration standards were diluted from the Agilent PAH analyzer calibration kit (part number G3440-85009) using isooctane. The kit contains a stock solution of 27 PAHs at 10 µg/mL and a stock solution of five ISTDs at 50 µg/mL. Twelve calibration levels were prepared: 0.1, 0.25, 0.5, 1, 2, 10, 20, 100, 200, 400, 750, and 1,000 ng/mL. Each level also contained 500 ng/mL of the ISTDs. See Table 2 and Figure 2 for compound identifications. All quantitative measurements were performed with Agilent MassHunter Quantitative Analysis software version 11.1.

A sample of commercial topsoil (Weaver Mulch, Coatesville, PA, USA) was dried at 120 °C overnight. Five grams of the dried soil were extracted with 30 mL dichloromethane/acetone (1:1 v/v) with agitation overnight. The extract was filtered, and the filtrate was reduced 7.5-fold in volume by evaporation. The resulting extract was used for the robustness experiments.

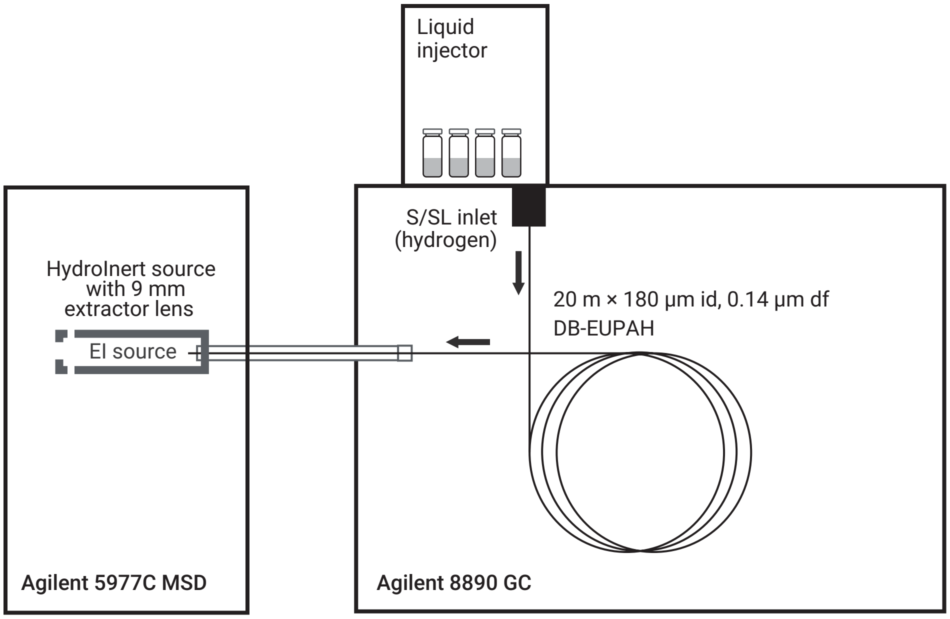

Figure 1. System configuration.

Table 1. GC and MS conditions for PAH analysis.

Method Parameters	
Inlet	EPC split/splitless
Mode	Pulsed splitless
Injection Pulse Pressure	40 psi until 0.70 min
Purge Flow to Split Vent	50 mL/min at 0.75 min
Injection Volume	1 µL
Inlet Temperature	320 °C
Inlet Liner	Agilent Universal Ultra Inert mid-frit liner (p/n 5190-5105)
Column	Agilent J&W DB-EUPAH, 20 m × 0.18 mm, 0.14 µm (p/n 121-9627)
Column Temperature Program	60 °C (1 min hold) 25 °C/min to 200 °C 10 °C/min to 335 °C (6 min hold) Total analysis time: 20 min
Carrier Gas and Flow Rate	H_2, 0.9 mL/min constant flow
MSD	HydroInert 9 mm
Transfer Line Temperature	320 °C
Ion Source Temperature	320 °C
Quadrupole Temperature	150 °C
EM Voltage Gain Mode	3
Mode	SIM
Tune	ETUNE.U

The soil extract used for the robustness test was deliberately chosen to have a high matrix content to challenge the system. Note that for soils with this level of organic content, further sample cleanup should be considered for routine analysis. The sample preparation used in this study was for test purposes only. Also, the extraction solvent (1:1 v/v dichloromethane/acetone) is not recommended for routine analysis with hydrogen carrier gas. Halogenated solvents such as dichloromethane may react with hydrogen in the hot injection port, forming low levels of HCl, which can degrade the liner and column head over time.

Table 2. SIM ions used for quantifier and qualifiers.

Name	RT (min)	Quantifier	Qualifier 1	Qualifier 2	Qualifier 3
Naphthalene-d_8	4.068	136	134	108	
Naphthalene	4.089	128	127	129	102
1-Methylnaphthalene	4.681	142	141	115	139
2-Methylnaphthalene	4.833	142	141	115	143
Biphenyl	5.215	154	153	76	155
2,6-Dimethylnaphthalene	5.236	156	141	155	115
Acenaphthylene	5.761	152	151	153	76
Acenaphthene-d_{10}	5.851	164	80		
Acenaphthene	5.889	153	154	151	155
2,3,5-Trimethylnaphthalene	6.075	170	155	169	153
Fluorene	6.380	166	165	163	167
Dibenzothiophene	7.424	184	185	139	152
Phenanthrene-d_{10}	7.552	188	189		
Phenanthrene	7.585	178	179	177	152
Anthracene	7.625	178	179	177	152
1-Methylphenanthrene	8.438	192	191	193	190
Fluoranthene	9.529	202	203	201	101
Pyrene	10.060	202	203	201	101
Benz[a]anthracene	12.611	228	226	229	114
Chrysene-d_{12}	12.731	240	236		
Chrysene	12.794	228	226	229	114
Benzo[b]fluoranthene	15.058	252	126		
Benzo[k]fluoranthene	15.114	252	126		
Benzo[j]fluoranthene	15.181	252	126		
Benzo[e]pyrene	15.821	252	253	126	250
Benzo[a]pyrene	15.927	252	253	250	126
Perylene-d_{12}	16.133	264	260		
Perylene	16.191	252	253	126	250
Dibenz[a,c]anthracene	18.020	278	279	139	138
Dibenz[a,h]anthracene	18.093	278	279	139	138
Indeno[1,2,3-cd]pyrene	18.093	276	138	277	137
Benzo[ghi]perylene	18.655	276	138	277	137

Results and discussion

Initial calibration

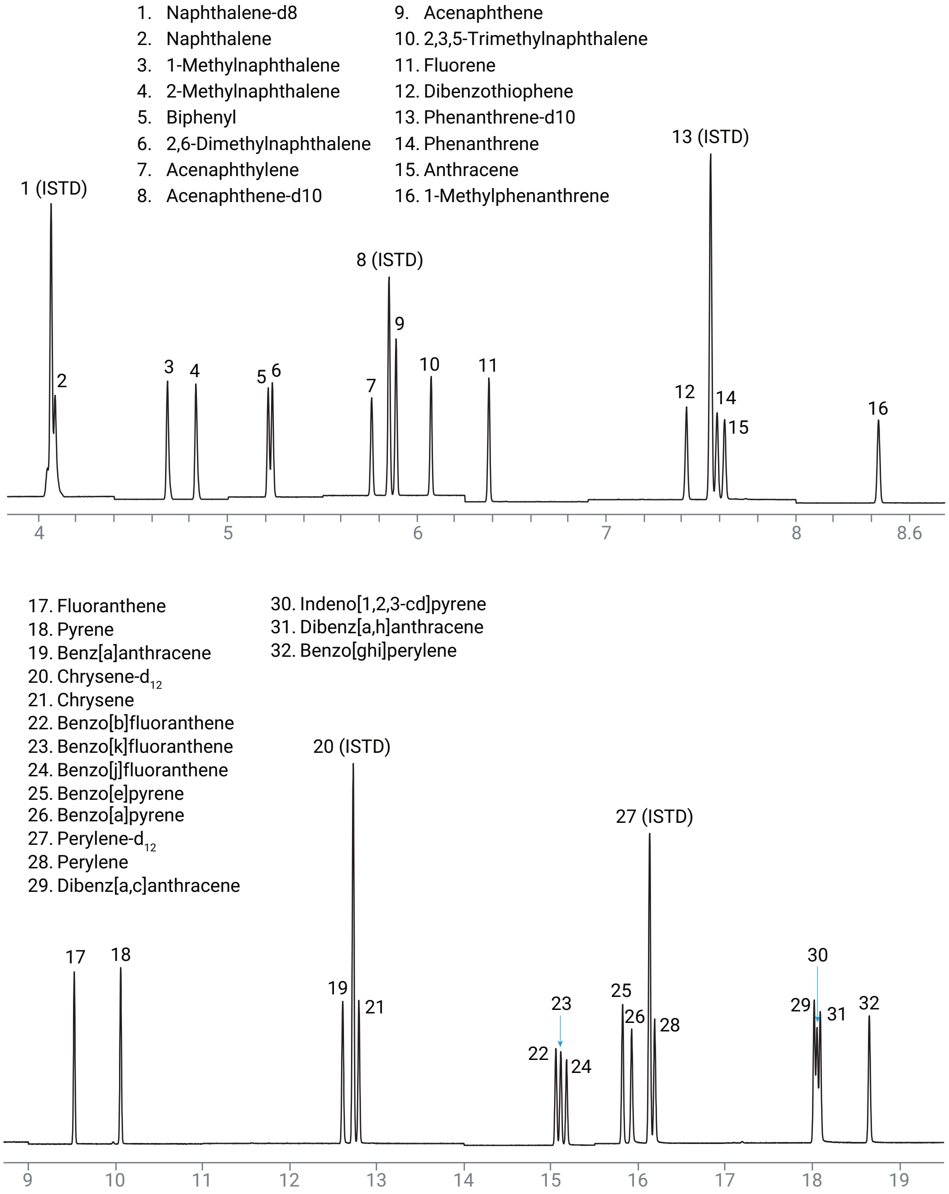

Figure 2. SIM TIC of the 100 pg/µL calibration standard with 500 pg/µL ISTDs.

Figure 2 shows the SIM TIC of the 100 pg/µL calibration standard with 500 pg/µL ISTDs. With the parameters used in this study, the peak shapes for PAHs, especially the later-eluting compounds, are excellent. The only exceptions are the first two peaks, naphthalene-d8 and naphthalene, which are somewhat distorted from the use of a pulsed injection. In general, the HydroInert source provides the best peak shapes for PAHs when using hydrogen carrier gas. The chromatographic resolution obtained with the current setup is also better than that obtained with helium.[2] Due to the combination of hydrogen carrier and a smaller diameter column, the run time with the current method is 20 minutes compared to 26 minutes for the helium method. The run time with the current method could have been reduced further and still maintain the same resolution as with the helium method. However, the 20-minute method conditions were chosen, as they give the best resolution of dibenz[a,c]anthracene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene.

Using the HydroInert source also resulted in excellent signal-to-noise ratios, allowing the calibration range to be extended to sub-picogram levels, as shown in Figure 3.

Eighteen of the 27 analytes had sufficient signal for calibration from 0.1 to 1,000 pg. Eight were calibrated from 0.25 to 1,000 pg. Only 1 compound, 2-methylnaphthalene, required calibration from 0.5 to 1,000 pg. Table 3 shows the calibration results of the system with 12 levels from 0.1 to 1,000 pg. All analytes show excellent linearity across the entire range.

If necessary, the relative standard error (RSE) value was used to guide removal of the lowest calibration points to achieve an RSE value of <20%. All calibrations had an R^2 value of 0.999 or greater.

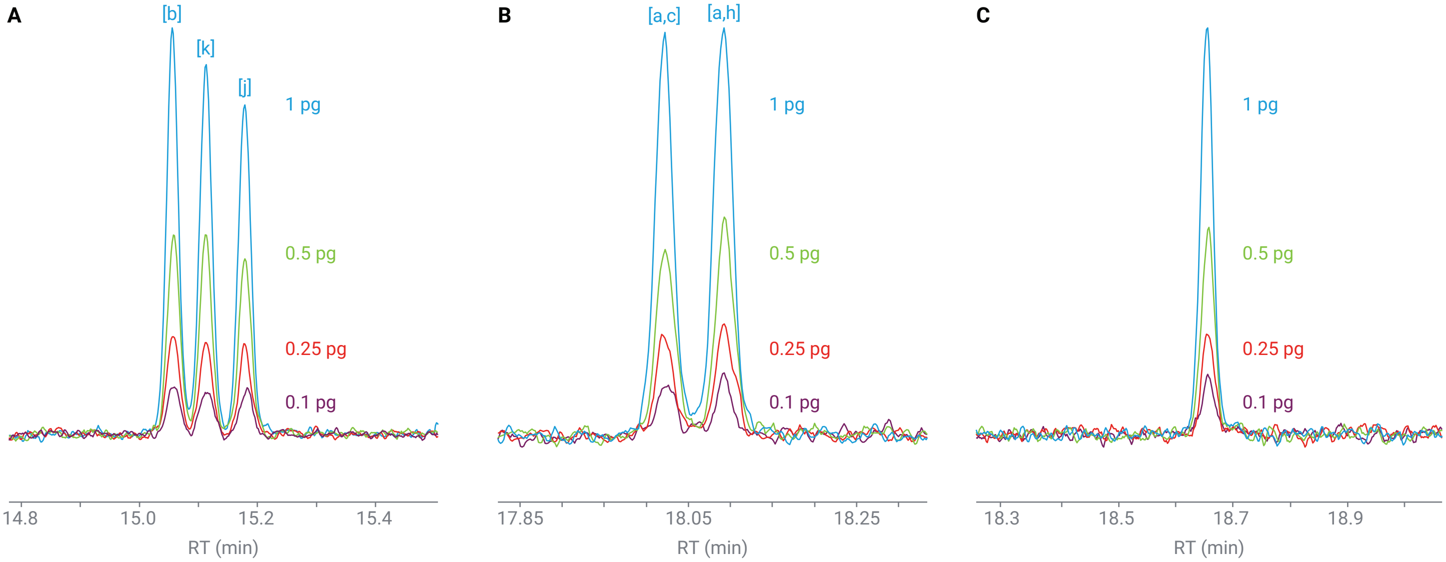

Figure 3. Response at quantifier ion for select compounds at the lowest calibration levels. (A) The [b], [k], and [j] isomers of benzofluoranthene. (B) The [a,c] and [a,h] isomers of dibenzanthracene. (C) Benzo[ghi]perylene.

Method detection limits

An MDL study was performed after completion of the initial calibration. Eight trials were performed with the 0.25 pg calibration standard. The calculated MDLs were obtained by applying the formula shown in Equation 1. For compounds with higher reporting limits, eight trials were performed at the concentration of 0.5 pg. Table 3 lists the calculated MDLs. The MDLs for the 27 compounds ranged from 0.03 to 0.20 pg.

Equation 1. Formula for MDL calculations.

MDL = s × t(n – 1, 1 – alpha = 99) = s × 2.998

Where:

t(n – 1, 1 – alpha) = t value for the 99% confidence level with n – 1 degrees of freedom

n = number of trials (8)

s = standard deviation of the eight trials

Stability of ISTD response over calibration range

One of the problems encountered when using helium carrier gas and the standard 3 mm extractor lens for the analysis of PAHs is the response of ISTDs climbing with increasing concentration of the analytes. This effect can cause the response of perylene-d_{12} to increase by as much as 60% over the calibration range and cause significant errors in quantitation. This problem has been addressed previously by using JetClean and a 9 mm extractor lens.[3,4] With JetClean, helium is used as the carrier gas, but hydrogen is continuously added to the source at a flow rate typically in the range of 0.2 to 0.35 mL/min. This approach greatly reduces the creeping ISTD effect and results in excellent quantitation.

Figure 4 shows the ISTD response stability over the calibration range with the current method. As demonstrated in Figure 4, the use of hydrogen carrier gas with the HydroInert source and 9 mm extractor lens also eliminates the creeping ISTD response problem. The %RSD for the raw area responses across the calibration range are all 3.3% or less. This is an important factor in achieving the excellent calibration linearity shown in Table 3.

Table 3. Results for 12 level SIM mode ISTD calibration over a range of 0.1 to 1,000 pg. All calibrations were linear fit with 1/x weighting.

Name	RT (min)	CF Limit Low (pg)	CF Limit High (pg)	CF R^2	Relative Standard Error	Avg. RF RSD	Conc. for MDL (pg)	MDL (pg)
Naphthalene-d$_8$ [ISTD]	**4.068**	**ISTD**						
Naphthalene	4.089	0.1	1,000	0.9998	5.7	23.0	0.50	0.19
1-Methylnaphthalene	4.681	0.25	1,000	0.9992	11.4	4.8	0.50	0.06
2-Methylnaphthalene	4.833	0.5	1,000	0.9992	10.9	7.6	0.50	0.07
Biphenyl	5.215	0.25	1,000	0.9991	11.1	9.7	0.50	0.18
2,6-Dimethylnaphthalene	5.236	0.25	1,000	0.9989	12.8	5.4	0.50	0.07
Acenaphthylene	5.761	0.25	1,000	0.9999	6.6	4.3	0.50	0.06
Acenaphthene-d$_{10}$ [ISTD]	**5.851**	**ISTD**						
Acenaphthene	5.889	0.25	1,000	0.9995	8.7	7.4	0.25	0.14
2,3,5-Trimethylnaphthalene	6.075	0.25	1,000	0.9997	13.8	12.6	0.50	0.20
Fluorene	6.380	0.25	1,000	0.9996	10.0	5.0	0.25	0.05
Dibenzothiophene	7.424	0.1	1,000	0.9998	7.6	16.9	0.25	0.09
Phenanthrene-d$_{10}$ [ISTD]	**7.552**	**ISTD**						
Phenanthrene	7.585	0.25	1,000	0.9998	6.2	5.3	0.25	0.10
Anthracene	7.625	0.1	1,000	0.9998	15.1	17.3	0.25	0.16
1-Methylphenanthrene	8.438	0.1	1,000	0.9996	8.5	4.9	0.25	0.10
Fluoranthene	9.529	0.1	1,000	0.9994	11.6	10.7	0.25	0.03
Pyrene	10.060	0.1	1,000	0.9993	11.3	16.4	0.25	0.06
Benz[a]anthracene	12.611	0.1	1,000	0.9998	8.3	19.8	0.25	0.03
Chrysene-d$_{12}$ [ISTD]	**12.731**	**ISTD**						
Chrysene	12.794	0.1	1,000	0.9999	6.2	19.3	0.25	0.06
Benzo[b]fluoranthene	15.058	0.1	1,000	0.9990	11.4	16.2	0.25	0.05
Benzo[k]fluoranthene	15.114	0.1	1,000	0.9993	13.1	18.5	0.25	0.06
Benzo[j]fluoranthene	15.181	0.1	1,000	0.9994	10.6	18.4	0.25	0.06
Benzo[e]pyrene	15.821	0.1	1,000	0.9996	9.3	16.2	0.25	0.09
Benzo[a]pyrene	15.927	0.1	1,000	0.9998	8.2	4.7	0.25	0.05
Perylene-d$_{12}$ [ISTD]	**16.133**	**ISTD**						
Perylene	16.191	0.1	1,000	0.9999	5.2	55.6	0.25	0.12
Dibenz[a,c]anthracene	18.020	0.1	1,000	0.9997	6.3	14.3	0.25	0.06
Dibenz[a,h]anthracene	18.093	0.1	1,000	0.9997	7.0	11.6	0.25	0.07
Indeno[1,2,3-cd]pyrene	18.093	0.1	1,000	0.9993	10.9	9.2	0.25	0.08
Benzo[ghi]perylene	18.655	0.1	1,000	0.9997	9.4	11.0	0.25	0.14

Stability of response with soil extract

Figure 5 shows the scan TIC of the soil extract and that of the solvent blank for comparison. As can be seen, the soil extract has a very high level of matrix and was chosen to challenge the system. For soils with this level of organic content, further sample cleanup would be recommended for routine analysis. The sample preparation used in this study was for test purposes only. Also, the extraction solvent (1:1 v/v dichloromethane/acetone) is not recommended for routine analysis with hydrogen carrier gas. Halogenated solvents like dichloromethane may react with hydrogen in the hot injection port, forming low levels of HCl, which can degrade the liner and column head over time.

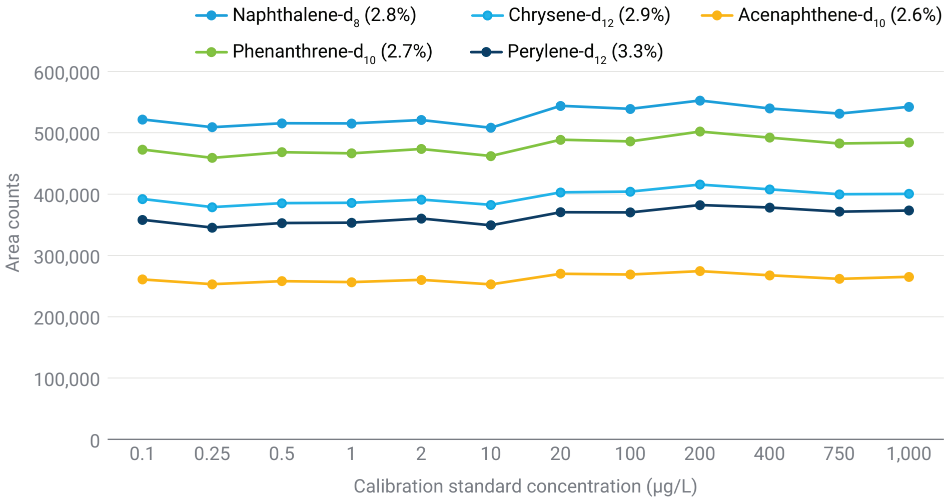

Figure 4. ISTD response stability over the calibration range.

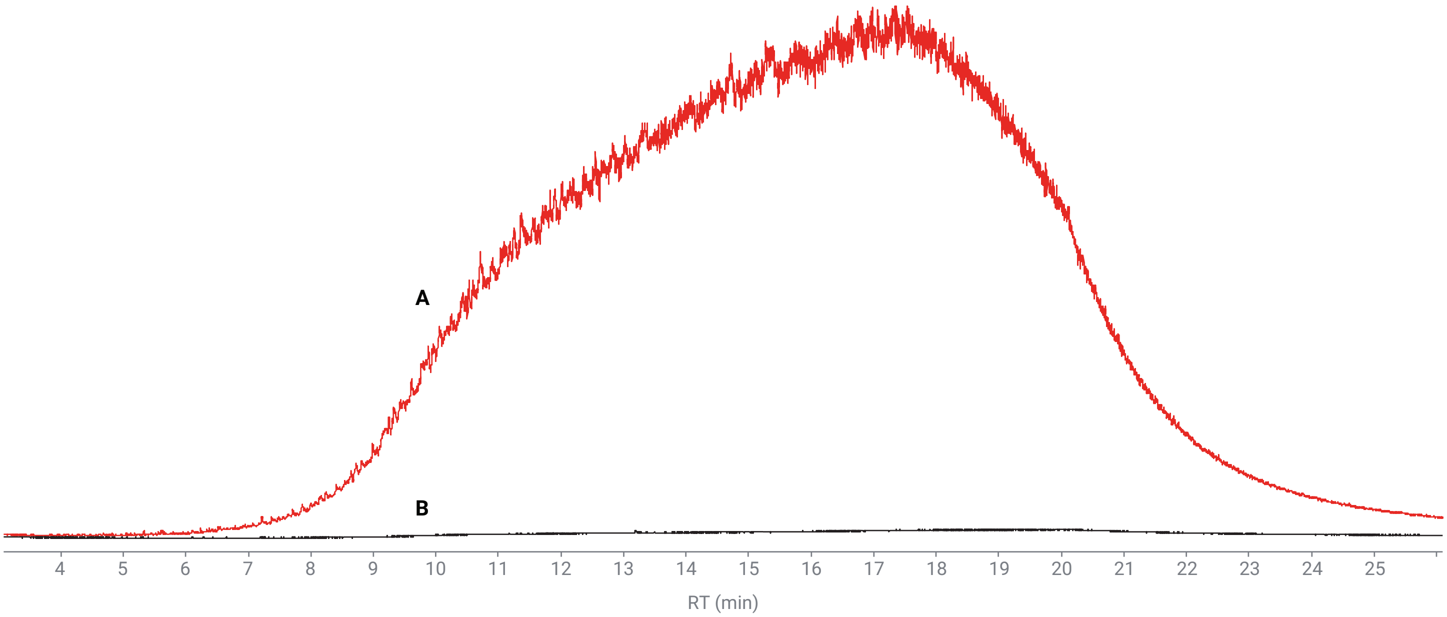

Figure 5. (A) Scan TIC of the soil extract. (B) Scan TIC of solvent blank for comparison.

Figure 6 shows the SIM TIC for the soil extract spiked with 100 ppb of the PAH standard and 500 ppb of the ISTDs. As seen in the SIM TIC, the soil matrix contributes a significant background signal in some of the time segments, the worst being the last segment. The extracted SIM 276 ion (quantifier for benzo[g,h,i]perylene) is also plotted to show that it is still suitable for quantitation.

Figure 7 shows the response stability of the measured concentrations for the PAHs in the spiked soil extract. No GC inlet or column maintenance was required during the 100 injection test. The gain curve for the electron multiplier was updated automatically every 15 runs during the sequence using a keyword. As seen in Figure 7, the results were stable over the 100 injections. The measured concentrations for all compounds fell within the range 92 to 131 pg.

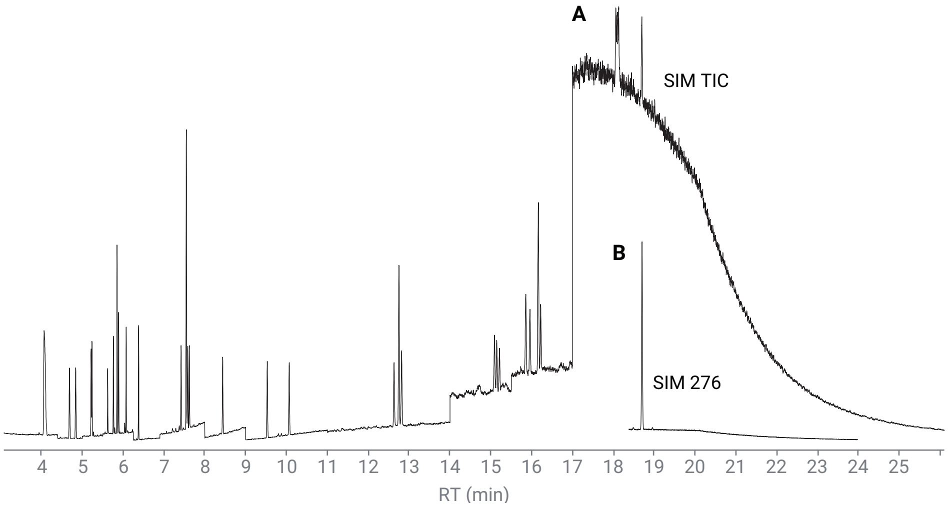

Figure 6. Soil extract spiked with 100 ppb PAH standard and 500 ppb ISTDs. (A) SIM TIC. (B) SIM 276 quantifier for benzo[g,h,i]perylene.

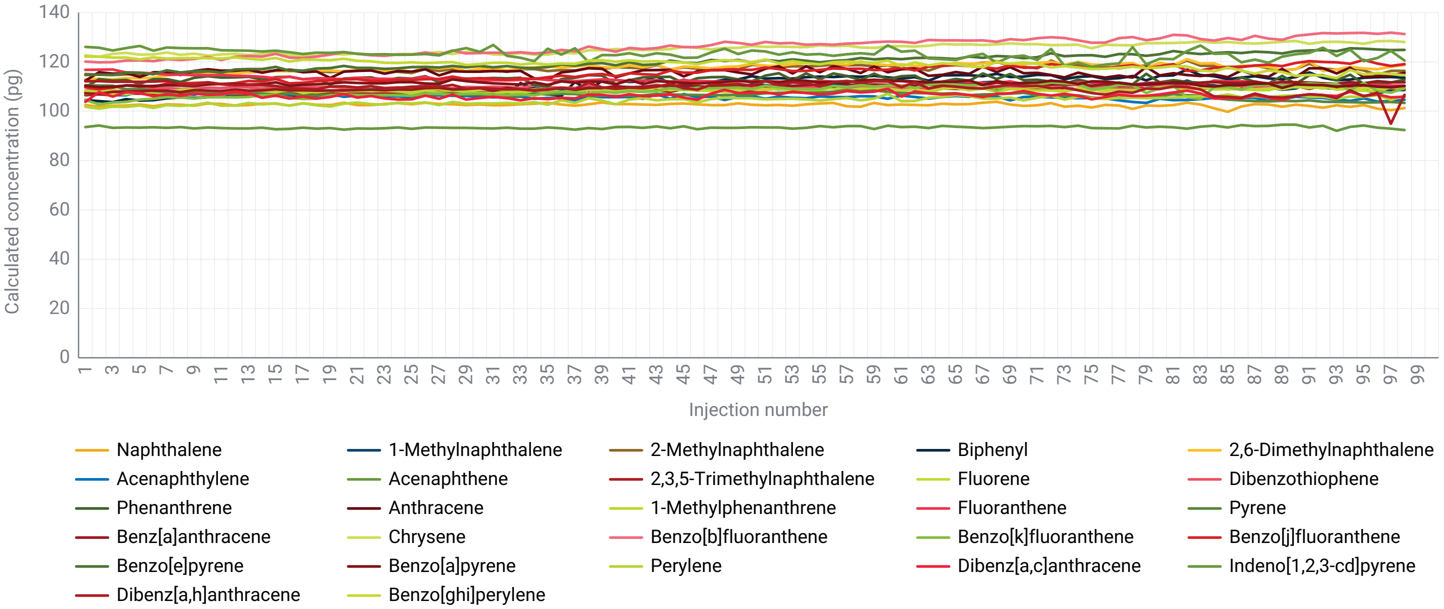

Figure 7. Stability of calculated concentrations over 100 injections of soil matrix spiked with 100 pg PAH standards and 500 pg ISTDs.

Conclusion

The described GC/MS method using hydrogen carrier gas and an Agilent HydroInert source demonstrated several improvements over previous helium methods:

- Excellent chromatographic peak shape with little or no tailing
- MDL and linearity comparable to or better than obtained with helium
- Better chromatographic resolution with a shorter run time
- ISTD response was stable across four orders of calibration
- Excellent linearity over <1 to 1,000 pg
- Average MDL ~0.1 pg
- Stable performance over 100 injections of a challenging soil extract

For laboratories looking to change their PAH analysis to the more sustainable hydrogen carrier gas, the HydroInert source with the 9 mm extractor lens enables the transition with equivalent or better performance.

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Safeguard Against Helium Uncertainty

Agilent HydroInert source for GC/MS with hydrogen carrier gas

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More Than Just Cost-Effective— Sustainable, Too

Even the most efficient GC systems consume their share of energy, gas, and other resources. The Agilent HydroInert source is just one innovation that is helping to change this equation.

Here are some other ways that partnering with Agilent can help your lab lower its energy and gas consumption.

Helium conservation module

This module bridges two electronic pneumatic control (EPC) channels to deliver a single carrier gas flow to your GC. That means you can use helium for your GC runs and switch to an alternate gas (such as nitrogen) when your GC is idle.

Electronic pneumatic control (EPC)

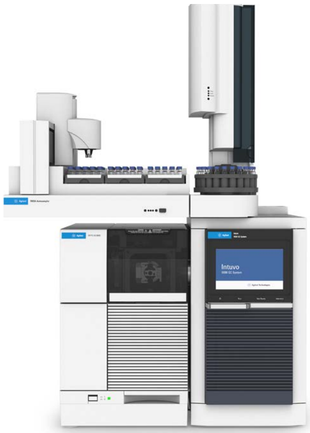
Agilent smart GC instruments feature core microchannel-based EPC, which protects against gas contaminants—such as particulates, water, and oils.

Direct column heating

The Agilent Intuvo 9000 GC uses an ultrafast and efficient direct heating system that requires less than half the electrical power of a conventional GC. It also significantly reduces the heat emitted back into the lab.

Conservation or conversion?

Ongoing helium shortages can cause unpredictability for GC analysts. Fortunately, there are ways to manage helium price fluctuations and delivery interruptions—and even use less gas.



Agilent Intuvo 9000 GC system

Agilent 8890 GC system

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