A rapid, sensitive, and consolidated method for PCBs and PAHs using GC-MS/MS

Authors

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Keywords

Polyaromatics hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), lower LOQ, PTV, sample preparation GC-MS, triple quadrupole, TSQ 9610, NeverVent Advanced Ionization ion source (AEI), TRACE 1610 GC

Goal

The purpose of the proposed method is to demonstrate the quantitative performance of the Thermo Scientific™ TSQ™ 9610 triple quadrupole GC-MS/MS system equipped with the Advanced Electron Ionization (AEI) source for the analysis of PAHs and PCBs in a single run.

Introduction

Polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) are toxic organic pollutants that can contaminate various food and environmental matrices, including soils, water, sun cream, and salmon. These compounds are produced because of natural and human processes. PCBs and PAHs are resistant to environmental degradation and can be transported over long distances. From the environment, they can enter the food chain where they are persistent and can bio-accumulate (vPvB).[1] GC-MS, and increasingly GC-MS/MS, are being utilized by analytical testing laboratories to analyze PAHs and PCBs. GC-MS/MS offers an increase in selectivity, allowing matrix interferences to be significantly reduced. This produces more confidence in sample results and allows an increase in productivity.

There are several challenges associated with the analysis of PAHs and PCBs in various matrices. First and foremost, the regulatory limits and requirements must be met consistently. Often separate methods are utilized, which adds to the number of analyses

per sample and reduces sample capacity. Sample preparation is also time consuming and requires a large sample volume to achieve the regulatory limits. One of the major challenges is the separation of the critical isobaric pairs of both PCBs and PAHs. Eliminating the overlap of such isobarics by chromatographic separation can lead to long analysis times, which can reduce the instrument productivity.

In this study, the TSQ 9610 triple quadrupole GC-MS/MS was used for the determination of PAHs and PCBs in water samples. The sample preparation procedure and chromatographic methods were chosen to reduce overall analysis time. Linearity and instrument detection limits (IDLs) were assessed in the experiments for all compounds, as well as an extended robustness study over the reproducibility of the detection of trace levels of PCBs and PAHs.

Experimental

Instrumentation

In the experiments described here, a TSQ 9610 triple quadrupole mass spectrometer equipped with a Thermo Scientific™ NeverVent™ Advanced Electron Ionization (AEI) ion source coupled to a Thermo Scientific™ TRACE™ 1610 gas chromatograph equipped with a Thermo Scientific™ AS 1310 autosampler and a Thermo Scientific™ iConnect™ programmable temperature vaporizing (iConnect-PTV). The TRACE 1610 GC with its instant connect injector and detector modules allows reconfiguration of the instrument to adapt to different workflows in minutes. The NeverVent technology allows for ion source cleaning, filament replacement, and column exchange without breaking instrument vacuum therefore ensuring minimum downtime to the laboratory workflow.

Chromatographic separation was achieved using a Thermo Scientific™ TraceGOLD™ TG-17SilMS column. The critical pairs of PAHs and PCBs include:

- PCB28 + PCB31
- Anthracene + Phenanthrene
- 2-Methylnaphthalene + 1-Methylnaphthalene
- Benzo[*a*]fluorene+ Benzo[*b*]fluorene
- Benzo[*a*]anthracene + Chrysene
- Benzo[*b*] + Benzo[*k*] + Benzo[*j*]fluoranthene
- Benzo[*e*] + Benzo[*a*]pyrene
- Dibenzo[*a,h*] + Dibenzo[*a,j*]acridine
- Dibenzo[*a,h*]anthracene + Indeno[1,2,3-*cd*]pyrene
- Dibenzo [*a,e*] + Dibenzo [*a,i*] + Dibenzo [*a,h*]pyrene

The column performance was such that the overall injection-to-injection time could be reduced to 24 min without sacrificing chromatographic separation. Table 1 shows the method conditions for the analysis.

Sample preparation

A conventional and straightforward LLE procedure was used to get the required 500 concentration factor:

5 mL of the extraction solvent (hexane, heptane, or cyclohexane) were added to 250 mL of water sample and mixed together. The extract was evaporated down to 500 µL and inserted in a 2 mL vial with 500 µL of acetonitrile. After vortexing, the vial was placed on the autosampler tray. Lower phase (acetonitrile) was injected.

Data acquisition, processing, and reporting

Data were acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, Integrated instrument control ensures full automation of the analytical workflow combined with an intuitive user interface for data analysis, customizable reporting, and storage in compliance with the Federal Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11).

Table 1. GC-MS/MS and autosampler experimental conditions for the analysis of PAHs and PCBs

Gas chromatography method	
Autosampler	AS 1610 (Injection technique: cold needle; Sample depth: bottom)
Gas chromatograph	TRACE 1610 GC with PTV injector
Liner	PTV Siltek metal liner, 2 x 2.75 x 120 mm (**P/N 45322044**)
Column	TraceGOLD TG-17SilMS, 30 m x 0.25 mm x 0.25 µm (**P/N 26072-1420**)
Injected solvent	Acetonitrile
Injection volume	2 µL
PTV temperature	Injection: 70 °C (0.10 min) Transfer: 2 °C/s → 340 °C (2 min) Cleaning: 13 °C/s → 360 °C (5 min), flow 30 mL/min
Carrier gas	He, 1.5 mL/min
GC oven program	70 °C, 1 min,
	45 °C/min to 200 °C,
	15 °C/min to 220 °C,
	3 °C/min to 227 °C,
	20 °C/min to 260 °C,
	30 °C/min to 316 °C, 0.50 min,
	1.5 °C/min to 319 °C,
	100 °C/min to 328 °C,
	100 °C/min to 340 °C, 10.20 min
	(Total run time 24 min)

Mass spectrometry method	
Instrument	TSQ 9610 triple quadrupole mass spectrometer
Ion source	AEI source (310 °C)
Ionization mode	Electron impact @ 35 eV
Acquisition type	T-SRM

Performance

To determine if the reduced sample volume of water had an effect on instrument sensitivity, standards were injected over a wide concentration range (0.4 µg/L to 300 µg/L).

Results and discussion

Chromatography

The method allowed all critical pairs to be separated, achieving the minimum required chromatographic resolution of 0.7. Figure 1 shows the separation of PCB 31 and PCB 28, Figure 2 shows the separation of anthracene and phenanthrene, and Figure 3 shows the separation of benzo[*b*] + benzo[*k*] + benzo[*j*]fluoranthene. Table 2 shows the resolution results for all critical separations.

Linearity and LOQs

The TSQ 9610 NeverVent AEI is equipped with the Thermo Scientific™ XLXR™ detector, which is an electron multiplier that offers extended detector lifetime and dynamic range. Calibration curves were produced in the range of 0.4 µg/L to 300 µg/L for the PAHs and PCBs. An appropriate internal standard was used to correct for potentially occurring matrix effects. All curves had a regression coefficient better than 0.990 and an amount deviation at LOQ of less than 35%. Figure 4 shows an example calibration curve for benzo[a]pyrene and the linearity for all compounds is summarized in Table 3.

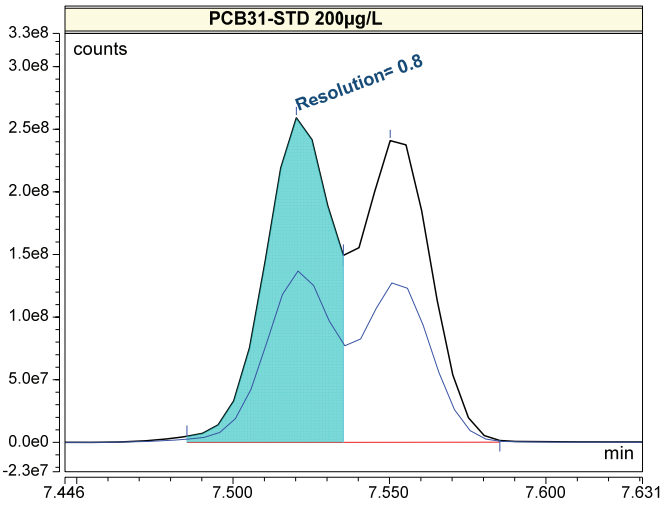


Figure 1. Separation of PCB 31 and PCB 28 at 200 µg/L

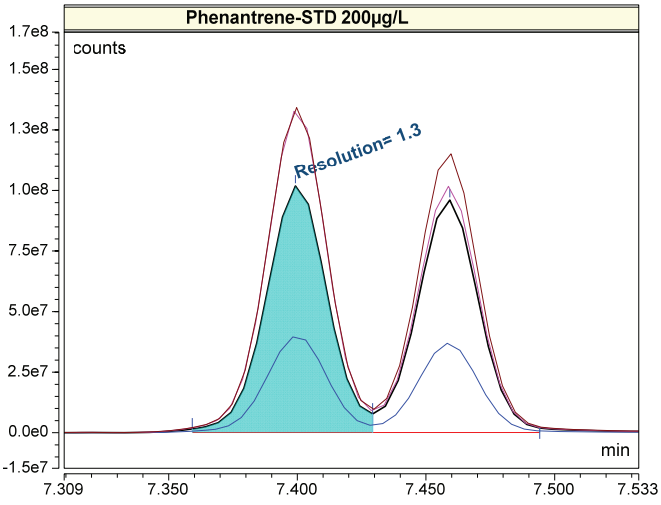


Figure 2. Separation of phenanthrene and anthracene at 200 µg/L

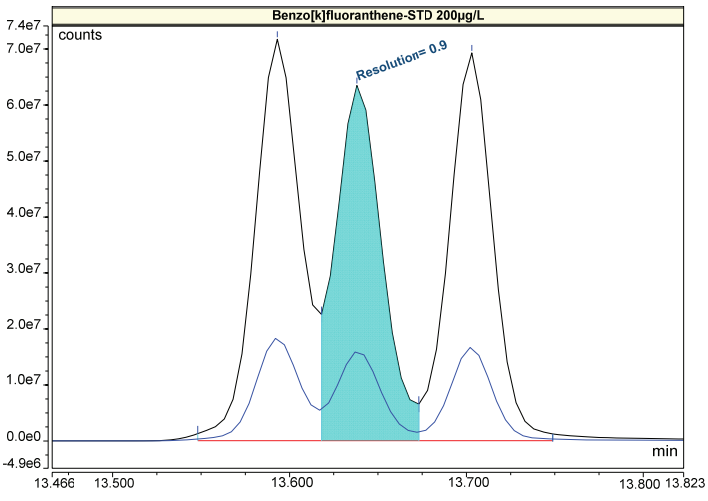


Figure 3. Separation of benzo[*b*] + benzo[*k*] + benzo[*j*]fluoranthene at 200 µg/L

All LOQs were found to be ≤ 0.4 µg/L. All compounds at this low level of detection showed consistent peak shape, good chromatographic resolution, and a signal-to-noise ratio well above the LOQ of 10, as reported in Figure 5 for a subset of compounds. Appropriate reproducibility results were observed after several consecutive injections of water sample extracts. To assess the reproducibility at the limit of quantitation, an extract spiked at 0.4 µg/L was injected 10 times (from the same vial) and RSD% values were calculated using internal standard calibration, demonstrating excellent reproducibility with typical RSDs of less than 25%. Table 4 shows results for all compounds.

Table 2. Chromatographic peak resolution – Calculated at 200 µg/L

Peak name	Resolution
2-Methylnaphthalene	2.7
1-Methylnaphthalene	
Phenanthrene	1.3
Anthracene	
PCB31	0.8
PCB28	
Benzo[*a*]fluorene	1.4
Benzo[*b*]fluorene	
Benzo[*a*]anthracene	2.3
Chrysene	
Benzo[*b*]fluoranthene	0.9
Benzo[*k*]fluoranthene	
Benzo[*k*]fluoranthene	1.4
Benzo[*j*]fluoranthene	
Benzo[*e*]pyrene	1.4
Benzo[*a*]pyrene	
Dibenzo[*a,h*]acridine	0.8
Dibenzo[*a,j*]acridine	
Dibenzo[*a,h*]anthracene	0.9
Indeno[1,2,3-*cd*]pyrene	
Dibenzo[*a,e*]pyrene	3.0
Dibenzo[*a,i*]pyrene	
Dibenzo[*a,i*]pyrene	1.5
Dibenzo[*a,h*]pyrene	

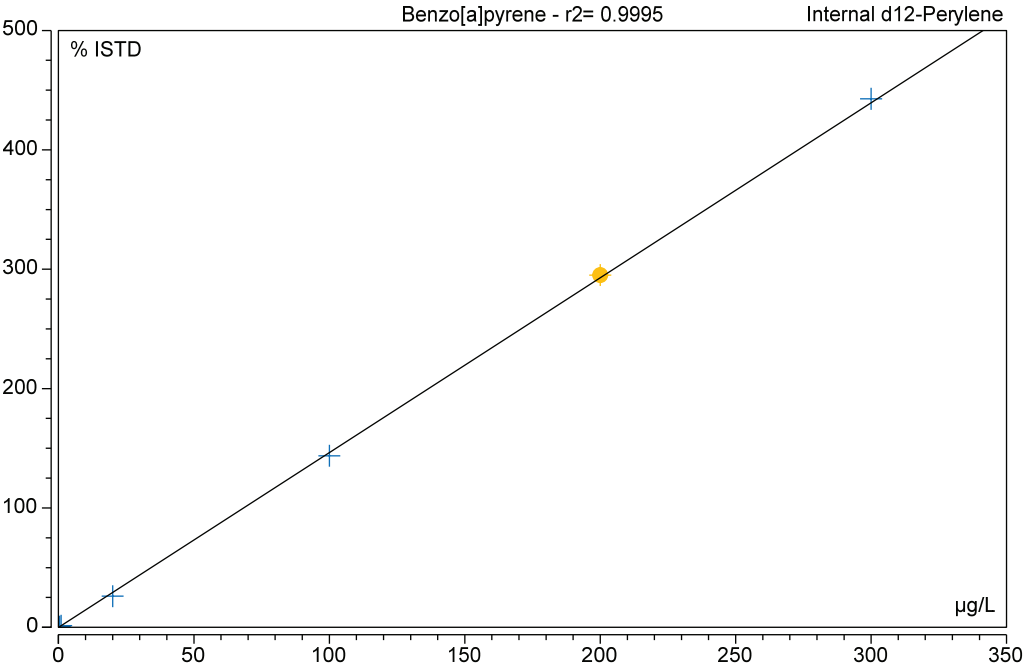
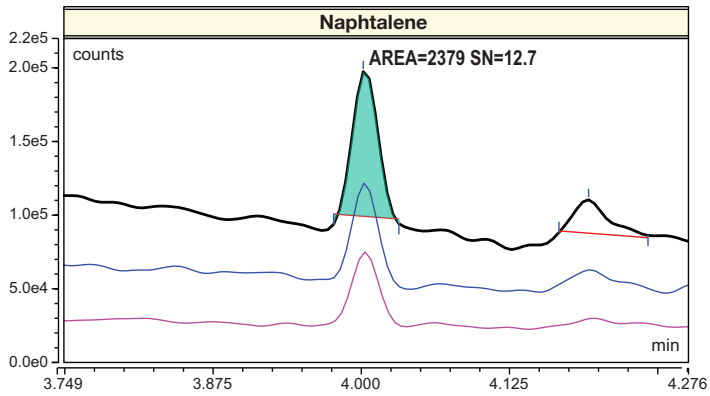


Figure 4. Calibration curve for benzo[*a*]pyrene. Six levels were used (0.4, 1, 20, 100, 200, 300 µg/L)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1.0e5
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0.0e0
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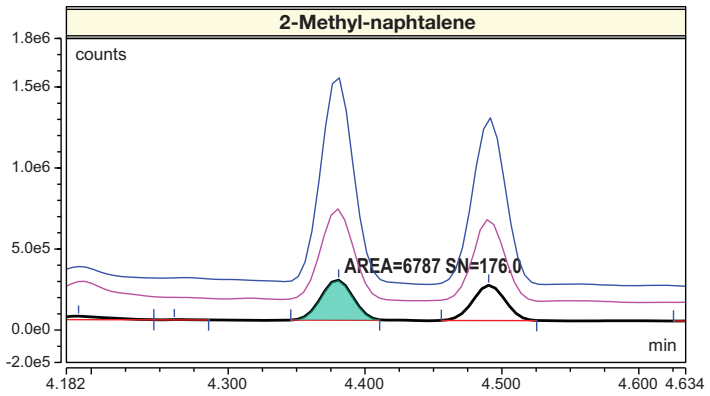
3.875
4.000
4.125
4.276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-2.0e5
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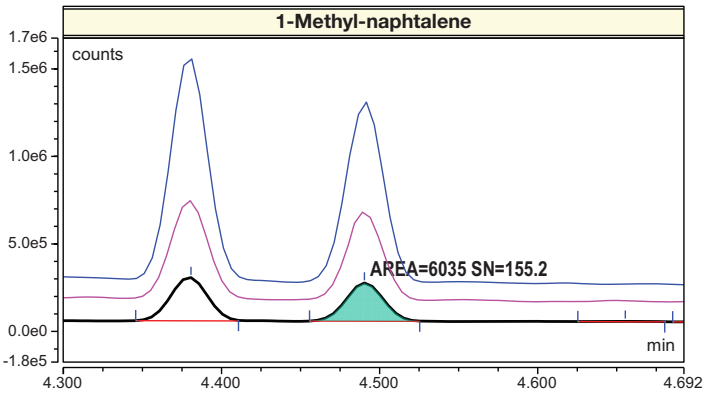
4.300
4.400
4.500
4.600
4.634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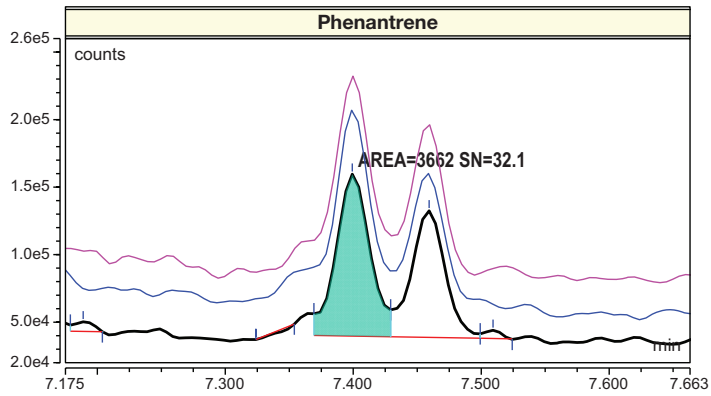
-1.8e5
4.300
4.400
4.500
4.600
4.692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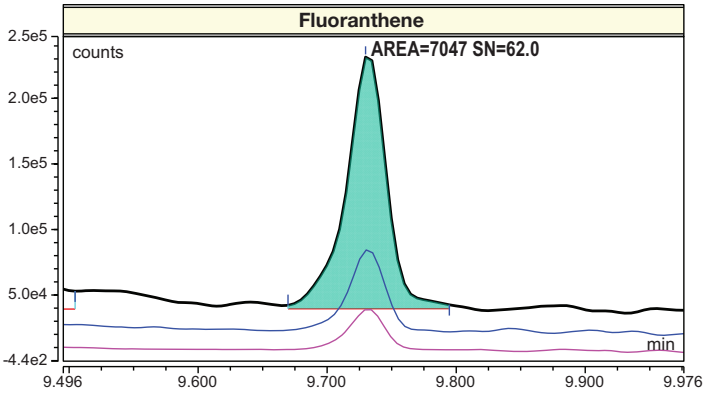
7.500
7.600
7.663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counts
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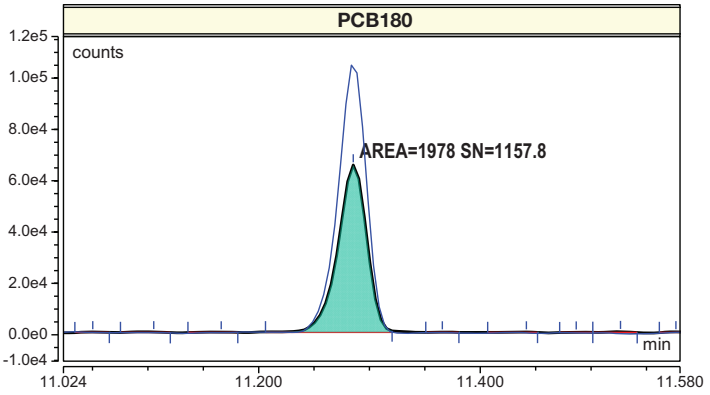
9.700
9.800
9.900
9.976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counts
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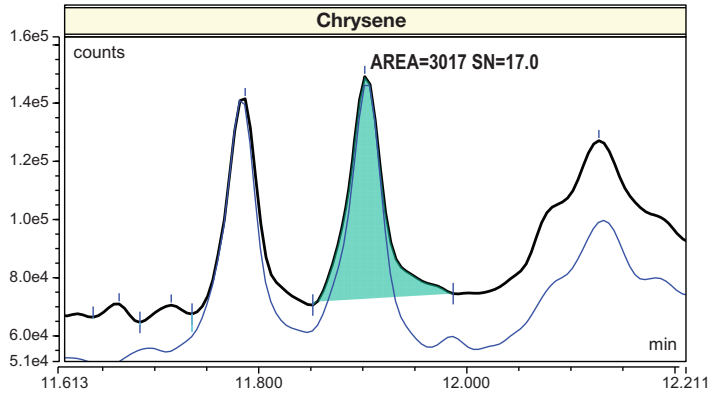
11.200
11.400
11.580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counts
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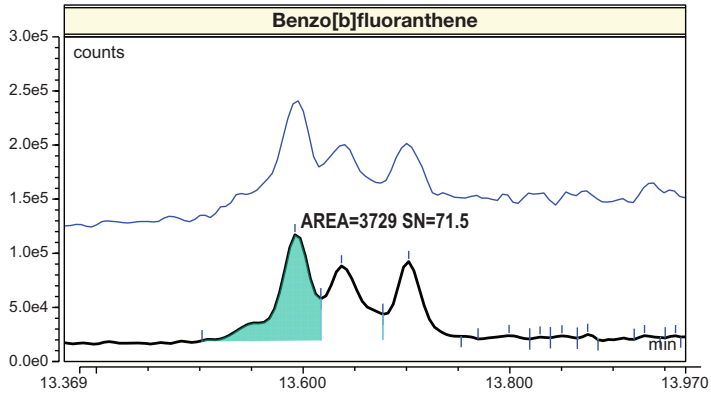
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counts
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13.970

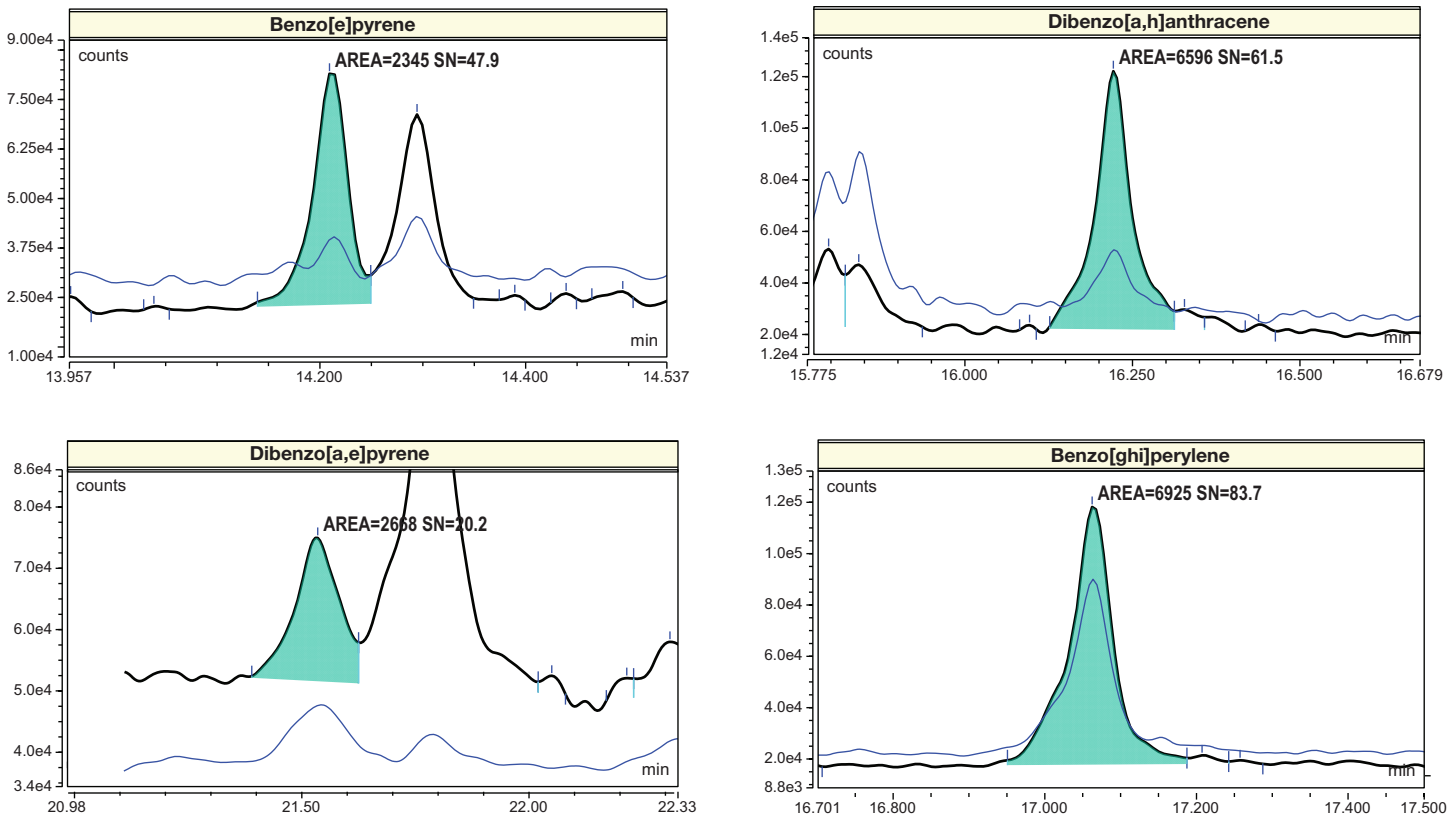

Figure 5. Overlaid SRM (quantifier ion in green, and qualifier ions in blue line) at 0.4 µg/L for a subset of analytes

Table 3. Analytical figures of merit (linearity, LOQ) obtained for all compounds under investigation in this study

Compound	ISTD	LOQ (µg/L)	Calibration type	R^2	%Dif.- LOQ
Naphthalene	d_8-Naphthalene	0.4	Lin, WithOffset, 1/A	0.9998	1.9
2-Methyl-naphthalene	d_8-Naphthalene			0.9997	6.5
1-Methyl-naphthalene	d_8-Naphthalene			0.9998	7.9
Acenaphthylene	d_{10}-Acenaphthene			0.9989	5.1
Acenaphthene	d_{10}-Acenaphthene			0.9999	9.7
Fluorene	d_{10}-Acenaphthene			0.9978	28.1
PCB18	d_{10}-Acenaphthene			0.9979	26.6
Phenanthrene	d_{10}-Phenanthrene			0.9997	5.2
Anthracene	d_{10}-Phenanthrene			0.9981	19.2
PCB31	PCB53			0.9992	12.5
PCB28	PCB53			0.9955	17.4
PCB52	PCB53			0.9995	15.1
PCB44	PCB53			0.9995	19.8
PCB101	PCB53			0.9990	21.4
Fluoranthene	d_{10}-Phenanthrene			0.9991	18.7
PCB149	PCB53			0.9989	13.7
PCB118	PCB53			0.9983	26.6
Pyrene	d_{12}-Chrysene			0.9995	9.1
PCB153	PCB53			0.9990	23.0
Benzo[*a*]fluorene	d_{12}-Chrysene			0.9963	-1.7
Benzo[*b*]fluorene	d_{12}-Chrysene			0.9950	9.0
PCB138	d_{12}-Chrysene			0.9996	1.1
PCB180	d_{12}-Chrysene			0.9996	4.0
PCB170	d_{12}-Chrysene			0.9996	3.3
Benzo[*a*]anthracene	d_{12}-Chrysene			0.9995	12.8
Chrysene	d_{12}-Chrysene			0.9997	12.0
Benzo[*b*]fluoranthene	d_{12}-Perylene			0.9990	3.6
Benzo[*k*]fluoranthene	d_{12}-Perylene			0.9998	15.0
Benzo[*j*]fluoranthene	d_{12}-Perylene			0.9990	11.5
Benzo[*e*]pyrene	d_{12}-Perylene			0.9997	6.8
Benzo[*a*]pyrene	d_{12}-Perylene			0.9995	8.5
3-Methylcholanthrene	d_{12}-Perylene			0.9988	24.7
Dibenzo[*a,h*]acridine	d_{14}-Dibenzo[*a,h*]anthracene			0.9997	5.0
Dibenzo[*a,j*]acridine	d_{14}-Dibenzo[*a,h*]anthracene			0.9988	17.6
Indeno[1,2,3-*cd*]pyrene	d_{14}-Dibenzo[*a,h*]anthracene			0.9989	18.5
Dibenzo[*a,h*]anthracene	d_{14}-Dibenzo[*a,h*]anthracene			0.9998	9.2
Benzo[*ghi*]perylene	d_{14}-Dibenzo[*a,h*]anthracene			0.9997	3.2
Dibenzo[*a,e*]pyrene	d_{12}-Coronene			0.9988	26.9
Dibenzo[*a,i*]pyrene	d_{12}-Coronene			0.9949	34.3
Dibenzo[*a,h*]pyrene	d_{12}-Coronene			0.9968	34.8

Table 4. Reproducibility for 10 replicate injections at 0.4 µg/L

Compound	RSD (%)
Naphthalene	5
2-Methylnaphthalene	3
1-Methylnaphthalene	3
Acenaphthylene	11
Acenaphthene	18
Fluorene	2
PCB18	3
Phenanthrene	3
Anthracene	5
PCB31	6
PCB28	5
PCB52	1
PCB44	2
PCB101	2
Fluoranthene	5
PCB149	5
PCB118	4
Pyrene	3
PCB153	3
Benzo[*a*]fluorene	23

Compound	RSD (%)
Benzo[*b*]fluorene	21
PCB138	3
PCB180	1
PCB170	6
Benzo[*a*]anthracene	9
Chrysene	10
Benzo[*b*]fluoranthene	8
Benzo[*k*]fluoranthene	4
Benzo[*j*]fluoranthene	4
Benzo[*e*]pyrene	4
Benzo[*a*]pyrene	8
3-Methylcholanthrene	17
Dibenzo[*a,h*]acridine	8
Dibenzo[*a,j*]acridine	7
Indeno[1,2,3-*cd*]pyrene	6
Dibenzo[*a,h*]anthracene	4
Benzo[*ghi*]perylene	4
Dibenzo[*a,e*]pyrene	6
Dibenzo[*a,i*]pyrene	6
Dibenzo[*a,h*]pyrene	7

Robustness

Robustness was assessed by injecting a QC standard in solvent at a concentration level of 0.4 µg/L (lowest calibration level) after every 10 samples (wastewater and drinking water) over 80 consecutive injections. During this sequence, the calculated concentration was consistent and the chromatographic resolution excellent. Figure 6 shows the calculated values for a subset of compounds over the 80-sequence injection, whereas Figure 7 shows the consistently excellent peak resolution over the extended run.

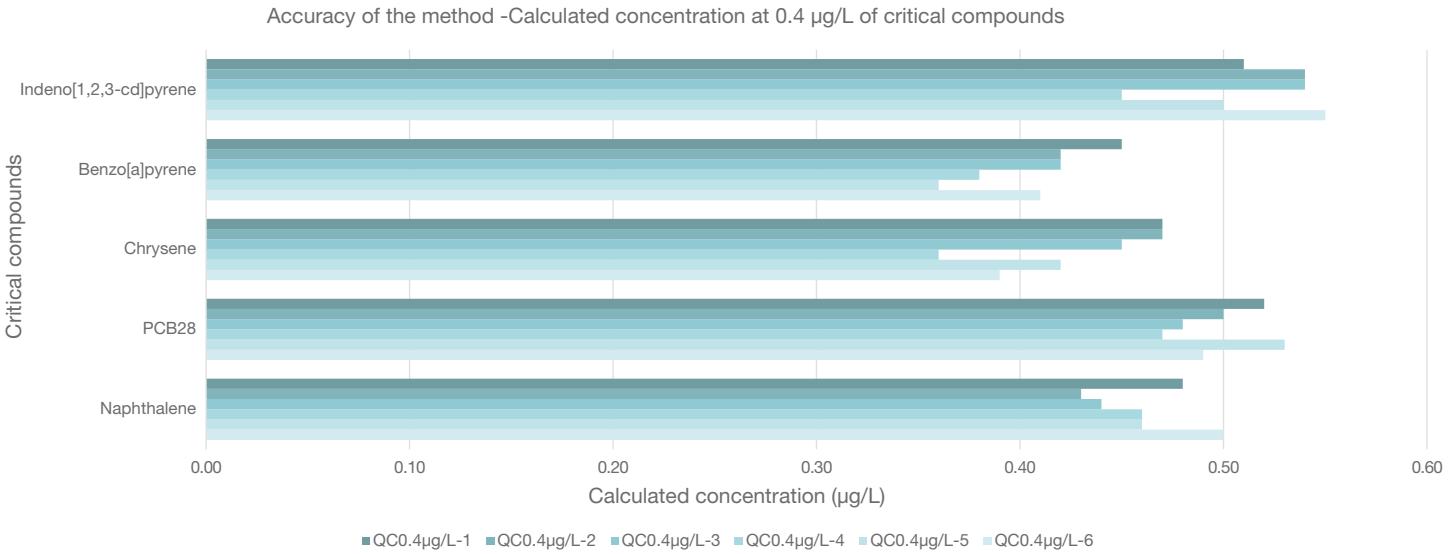

Figure 6. Robustness of the calculated amount of a QC at 0.4 µg/L injected at intervals over 80 injections for subset target compounds

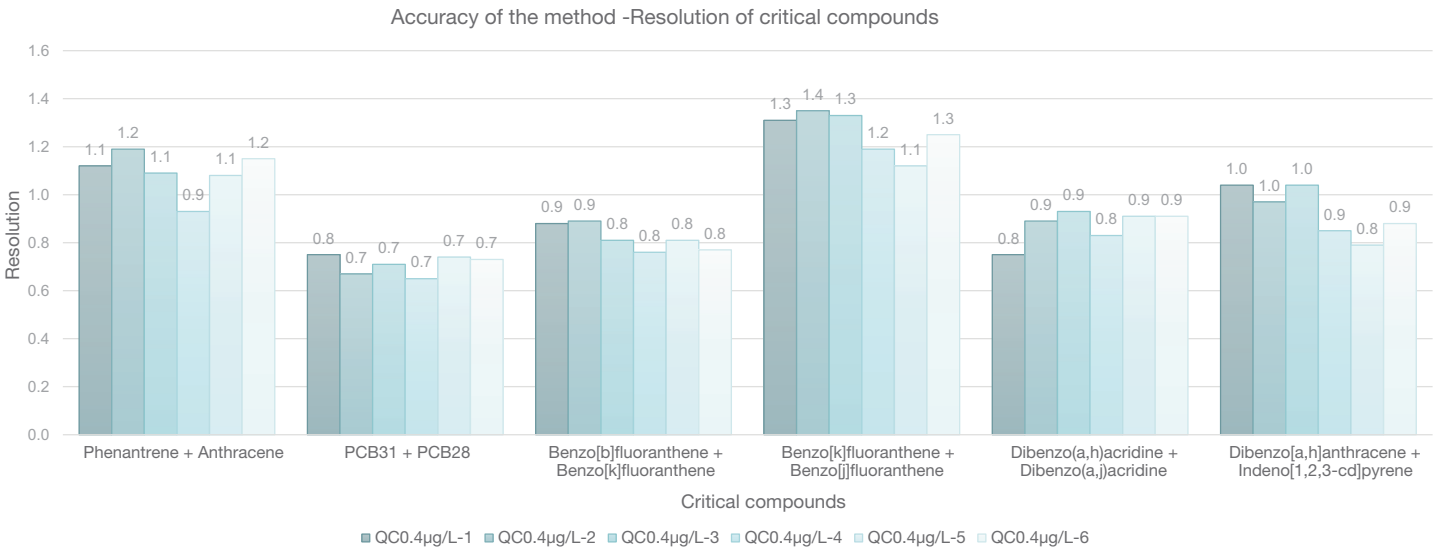

Figure 6. Robustness of the calculated amount of a QC at 0.4 µg/L injected at intervals over 80 injections for subset target compounds

Conclusion

The results obtained in these experiments demonstrate that the TSQ 9610 mass spectrometer equipped with the NeverVent AEI ion source in combination with the TRACE 1610 GC and the AI/AS 1610 liquid autosampler delivers consistent and reliable analytical performance for analysis of PAHs and PCBs in water samples.

- The high selectivity of the TraceGOLD-17SilMS column allowed chromatographic separation of the target analytes in less than 24 minutes. All isobaric compounds were separated.
- The XLXR detector allowed for extended linearity over a concentration range 0.4 µg/L to 300 µg/L for the PAHs and PCBs with coefficients of determination of R^2 >0.99 and AvCF % RSDs at first calibration level <35%.
- The engineered design and improved sensitivity of the NeverVent AEI ion source allows to achieve limits of quantification as low as 0.4 µg/L with consistent results at this level.

Reference

1. Guidance on information requirements and chemical safety assessment, part C: PBT/vPvB. [Online] https://echa.europa.eu/documents/10162/13643/information_requirements_part_c_en.pdf (accessed May 8, 2018)

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