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Simple, fast and sensitive method to analyze up to 40 PAHs and PCBs in a single GC-MS/MS run

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Goal

This method demonstrates the quantitative performance of the Thermo Scientific™ TSQ™ 9000 triple quadrupole GC-MS/MS system equipped with the Advanced Electron Ionization (AEI) source for the routine analysis of PAHs and PCBs in a single run, based on a quick, sensitive and robust workflow which increases coverage and improves turnaround time, while eliminating the need for large sample volumes, thus reducing the amount of extraction solvent used, as well as sample preparation time and storage.

Introduction

Polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are toxic organic compounds. Contract testing laboratories (CTLs) utilize multiple strategies to analyze these compound classes in various matrices (e.g., soil, food, wastewater, lotions, etc.). Diverse industries including cosmetics, food and environmental testing labs are invested in the analysis of PAHs.

Gas chromatography-mass spectrometry (GC-MS) is well suited for the analysis of PAHs and PCBs. With the increased presence of triple quadrupole GC-MS/MS mass spectrometers in laboratories, selectivity can be increased in comparison to classical detectors (e.g., ECD, FID). This results in the ability to cut through chemical background (interference) and enhances the capability and productivity of testing laboratories while maintaining the low quantification limits that are required by regulatory requirements.

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A common testing method using GC-MS can identify 7 PCBs and 16 PAHs, from naphthalene to Benzo[g,h,i] perylene, covering a range of boiling points (BP) from 218 °C to 550 °C, respectively. By incorporating the Thermo Scientific™ Instant Connect Programmable Temperature Vaporizing (PTV) Injector and a specialized column (30 m x 0.25 mm x 0.25µm), this range can be extended to include compounds with even higher BP, as well as the analysis of the critical pair "Dibenzo[a,e],[a,i] and [a,h]pyrene", which are typically analyzed in LC-based methods.

This application brief describes a highly productive analysis of PAHs and PCBs (Table 1) in water samples through a consolidated GC-MS/MS method using the Thermo Scientific™ TRACE™ 1310 GC and the TSQ 9000 triple quadrupole GC-MS/MS. The method is characterized by a shorter analysis time and increased coverage for both PCBs and PAHs in a single run with good resolution and low LOQs in accordance with regulatory limits. At the same time, it uses a reduced volume of water sample, resulting in less solvent needed during the extraction step of the sample preparation, while ensuring good robustness and increased productivity of the method. This note will also cover smart software tools that are integrated into the analysis workflow to minimize the time needed to implement and maintain the methodology in routine testing.

This new method was developed to reduce the overall lab workload for the analysis of targeted compounds with a simplified sample preparation and a single analysis. For the entire list of compounds in Table 1 to be analyzed effectively, the TRACE 1310 GC and an innovative column chemistry were used to optimize the chromatographic separation of critical isomer pairs (Table 2). The column performance was such that the overall injection-to-injection

Table 1. Target PAH and PCB compounds

Compound	CAS	Compound	CAS
Naphthalene	91-20-3	PCB-138	35065-28-2
2-Methylnaphthalene	91-57-6	PCB-180	35065-29-3
1-Methylnaphthalene	90-12-0	PCB-170	35065-30-6
Acenaphthylene	208-96-8	Benzo[a]anthracene	56-55-3
Acenaphthene	83-32-9	Chrysene	218-01-9
Fluorene	86-73-7	Benzo[b]fluoranthene	205-99-2
PCB-18	37680-65-2	Benzo[k]fluoranthene	207-08-9
Phenanthrene	85-01-8	Benzo[j]fluoranthene	205-82-3
Anthracene	120-12-7	Benzo[e]pyrene	192-97-2
PCB-31	16606-02-3	Benzo[a]pyrene	50-32-8
PCB-28	7012-37-5	3-MethylCholanthrene	56-49-5
PCB-52	35693-99-3	Dibenzo[a,h]acridine	226-36-8
PCB-44	41464-39-5	Dibenzo[a,j]acridine	224-42-0
PCB-101	37680-73-2	Indeno[1,2,3-cd]pyrene	193-39-5
Fluoranthene	206-44-0	Dibenzo[a,h]anthracene	53.-70-3
PCB-149	38380-04-0	Benzo[g,h,i]perylene	191-24-2
PCB-118	31508-00-6	Dibenzo[a,e]pyrene	192-65-4
Pyrene	129-00-0	Dibenzo[a,i]pyrene	189-55-9
PCB-153	35065-27-1	Dibenzo[a,h]pyrene	189-64-0
Benzo[a]fluorene	238-84-6		
Benzo[b]fluorene	243-17-4		

time could be reduced to 24 min without sacrificing chromatographic separation. Resolution of critical isomer pairs has been monitored over more than 80 injections of water (both raw water and wastewater) extracts. The selectivity of the TSQ 9000 GC-MS/MS equipped with Advanced Electron Ionization (AEI) source was used to reach the required lowered limit of quantification.

Method

Sample preparation

Labs that are testing for PAHs and PCBs are challenged by tedious, time-consuming and costly sample preparation steps, as well as the need to concentrate large sample volumes of water to reach the regulatory LOQ levels. Further, long chromatographic separations (>35 min per sample) and separate methods are often required, which negatively affect turnaround time and significantly increase the cost per sample.

In order to anticipate the reduced volume of water, standards were injected over a wide concentration range (0.4µg/L to 300µg/L).

Table 2: Compound isomers requiring critical chromatographic separation

Isomer 1	Isomer 2	Isomer 3
PCB-28	PCB-31	-
Anthracene	Phenanthrene	-
2-Methylnaphthalene	1-Methylnaphthalene	-
Benzo[a]fluorene	Benzo[b]fluorene	-
Benzo[a]anthracene	Chrysene	-
Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[j]fluoranthene
Benzo[e]pyrene	Benzo[a]pyrene	-
Dibenzo[a,h]acridine	Dibenzo[aj]acridine	-
Dibenzo[a,h]anthracene	Indeno[1,2,3-cd]pyrene	-
Dibenzo[a,e]pyrene	Dibenzo[a,i]pyrene	Dibenzo[a,h]pyrene

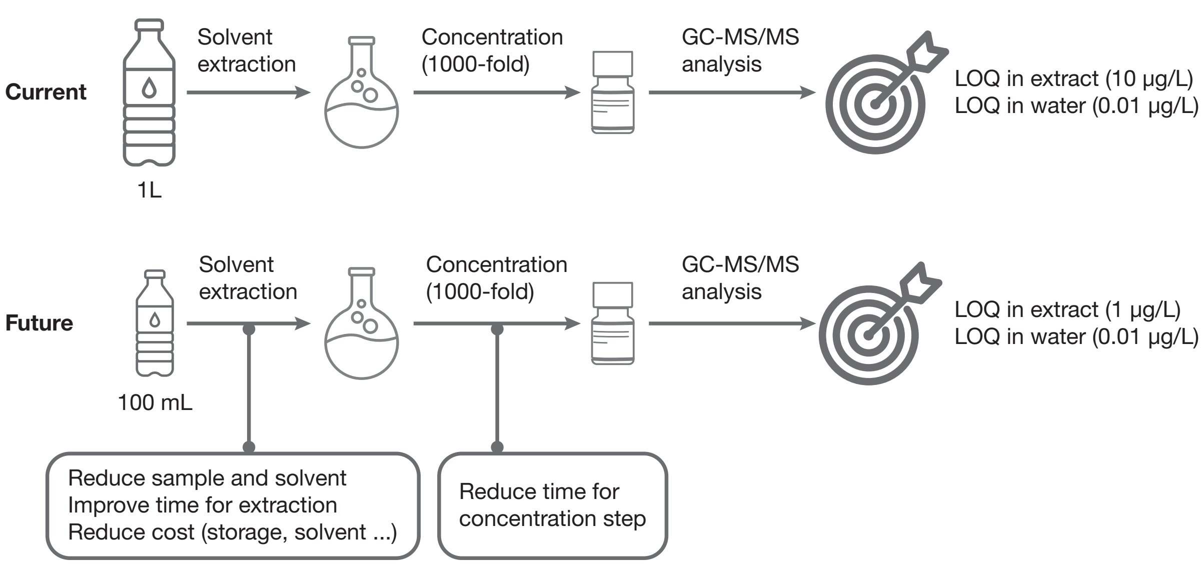


Figure 1. Comparison of conventional and improved water sample preparation workflow

Gas chromatography and mass spectrometry
TRACE 1310 GC with PTV Injector
Thermo Scientific™ PTV Siltek Metal Liner, 2 x 2.75 x 120 mm (P/N 45322044)

Injection volume	2 µL (MeCN)
Injector temperature	70°C to 360°C
Column flow	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 23.982 min)

Figure 2. TSQ 9000 with AEI source

Results and discussion

Linearity

Calibration curves were generated in the range of 0.4 µg/L to 300 µg/L for the PAHs and PCBs. The curves were corrected with an appropriate internal standard (ITSD), as shown in Table 3. All curves had a regression coefficient higher than 0.990 and an amount deviation at LOQ (0.4 ug/L) less than 20% , using a linear with offset (1/A) calibration type.

Table 3. Calibration curves for PAH and PCB compounds

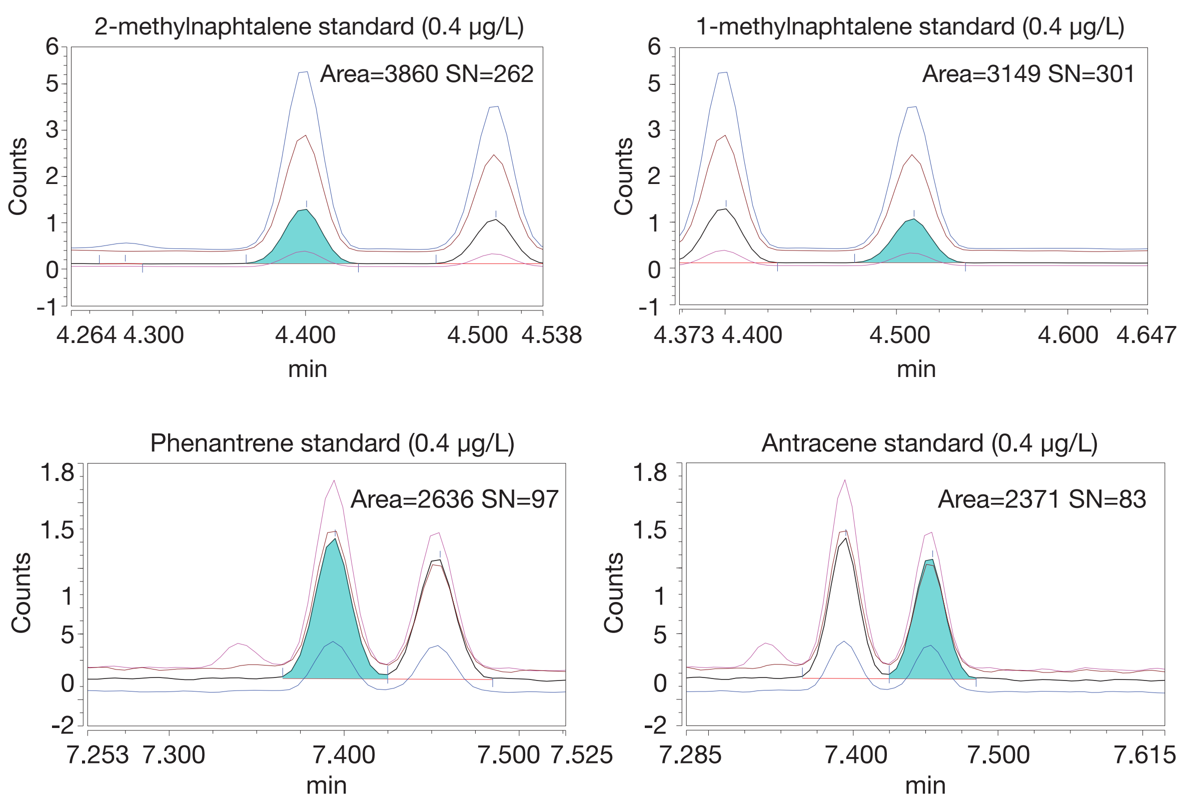
Compound	ISTD	R^2	Difference (%) - LOQ
Naphthalene	Napthalene-d8	0.9997	0.2
2-Methylnaphthalene	Napthalene-d8	0.9995	3.2
1-Methylnaphthalene	Napthalene-d8	0.9997	0.8
Acenaphthylene	Acenaphthene-d10	0.9998	4.5
Acenaphthene	Acenaphthene-d10	0.9997	-5.8
Fluorene	Acenaphthene-d10	0.9999	-1.6
PCB-18	Acenaphthene-d10	0.9997	-2.5
Phenanthrene	Phenanthrene-d10	0.9995	-3.6
Anthracene	Phenanthrene-d10	0.9996	-4.1
PCB-31	PCB-53	0.9990	0.8
PCB-28	PCB-53	0.9990	-3.0
PCB-52	PCB-53	0.9996	-0.8
PCB-44	PCB-53	1.0000	-4.1
PCB-101	PCB-53	0.9999	-7.0
Fluoranthene	Phenanthrene-d10	0.9979	-15.5
PCB-149	PCB-53	0.9985	-8.0
PCB-118	PCB-53	0.9984	-10.4
Pyrene	Chrysene-d12	0.9976	-1.8
PCB-153	PCB-53	0.9981	-14.2
Benzo[a]fluorene	Chrysene-d12	0.9993	-6.6
Benzo[b]fluorene	Chrysene-d12	0.9993	-8.1

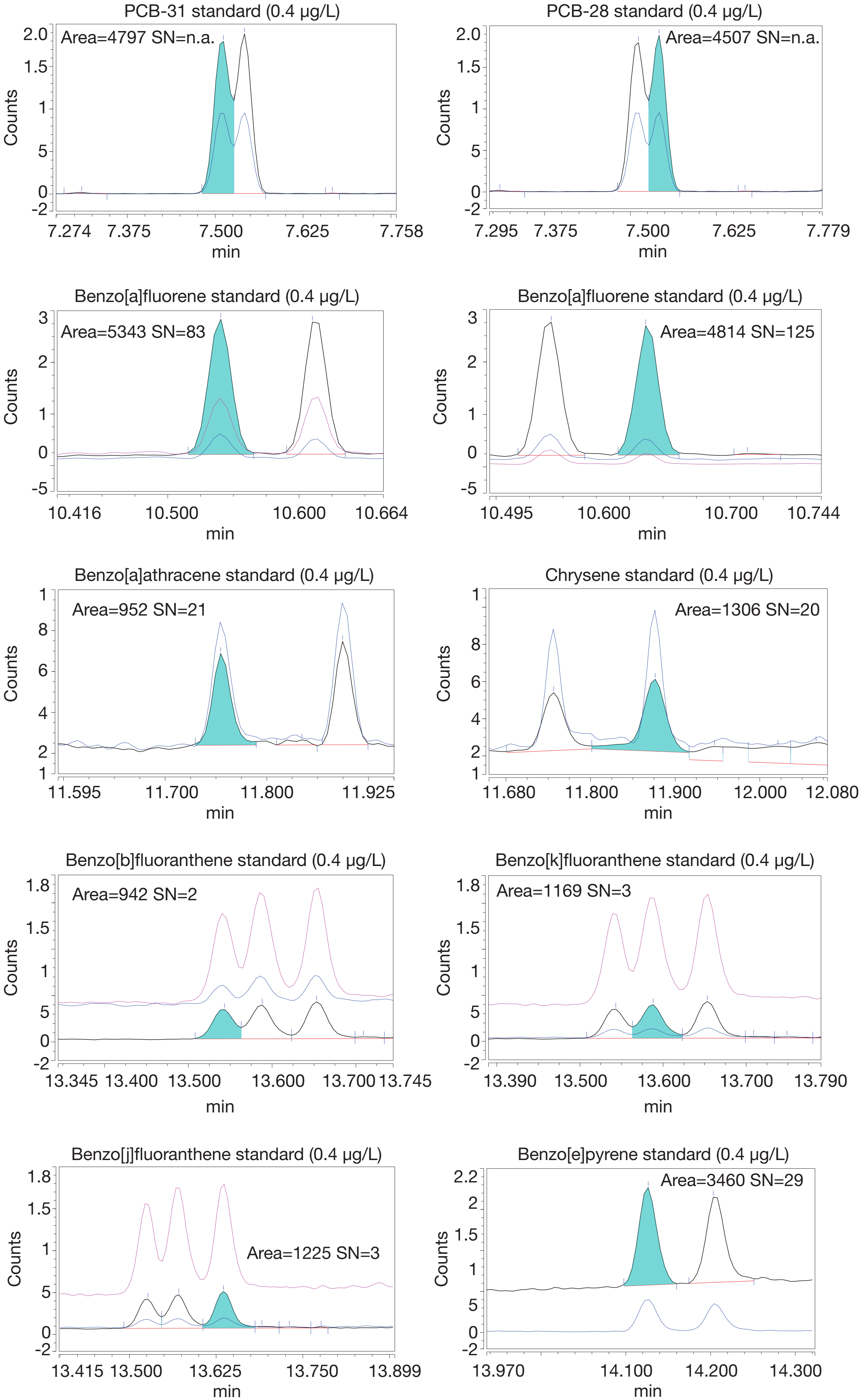
Table 3. Calibration curves for PAH and PCB compounds (continued)

Compound	ISTD	R2	Difference (%) - LOQ
PCB-138	Chrysene-d12	0.9984	-1.1
PCB-180	Chrysene-d12	0.9992	-3.0
PCB-170	Chrysene-d12	0.9996	-8.0
Benzo[a]anthracene	Chrysene-d12	0.9997	-10.4
Chrysene	Chrysene-d12	0.9996	4.8
Benzo[b]fluoranthene	Perylene-d12	0.9988	-10.5
Benzo[k]fluoranthene	Perylene-d12	0.9994	-4.3
Benzo[j]fluoranthene	Perylene-d12	0.9996	-7.2
Benzo[e]pyrene	Perylene-d12	0.9997	-2.1
Benzo[a]pyrene	Perylene-d12	0.9997	-11.8
3-methyl cholanthrene	Perylene-d12	0.9995	14.2
Dibenzo[a,h]acridine	Dibenzo[a,h]anthracene-d14	0.9998	7.2
Dibenzo[a,j]acridine	Dibenzo[a,h]anthracene-d14	0.9990	-4.2
Indeno[1,2,3-cd]pyrene	Dibenzo[a,h]anthracene-d14	0.9990	-5.3
Dibenzo[a,h]anthracene	Dibenzo[a,h]anthracene-d14	0.9998	-4.3
Benzo[ghi]perylene	Dibenzo[a,h]anthracene-d14	0.9997	-0.6
Dibenzo[a,e]pyrene	Coronene-d12	0.9995	11.9
Dibenzo[a,i]pyrene	Coronene-d12	0.9993	16.2
Dibenzo[a,h]pyrene	Coronene-d12	0.9998	14.1

Sensitivity

The following chromatograms present all critical compounds at the very low level of 0.4µg/L, demonstrating good resolution, peak shape and signal-to-noise ratio (Figure 3).





PCB-31 standard (0.4 µg/L)
Area=4797 SN=n.a.
PCB-28 standard (0.4 µg/L)
Area=4507 SN=n.a.
Benzo[a]fluorene standard (0.4 µg/L)
Area=5343 SN=83
Benzo[a]fluorene standard (0.4 µg/L)
Area=4814 SN=125
Benzo[a]athracene standard (0.4 µg/L)
Area=952 SN=21
Chrysene standard (0.4 µg/L)
Area=1306 SN=20
Benzo[b]fluoranthene standard (0.4 µg/L)
Area=942 SN=2
Benzo[k]fluoranthene standard (0.4 µg/L)
Area=1169 SN=3
Benzo[j]fluoranthene standard (0.4 µg/L)
Area=1225 SN=3
Benzo[e]pyrene standard (0.4 µg/L)
Area=3460 SN=29
Counts
min

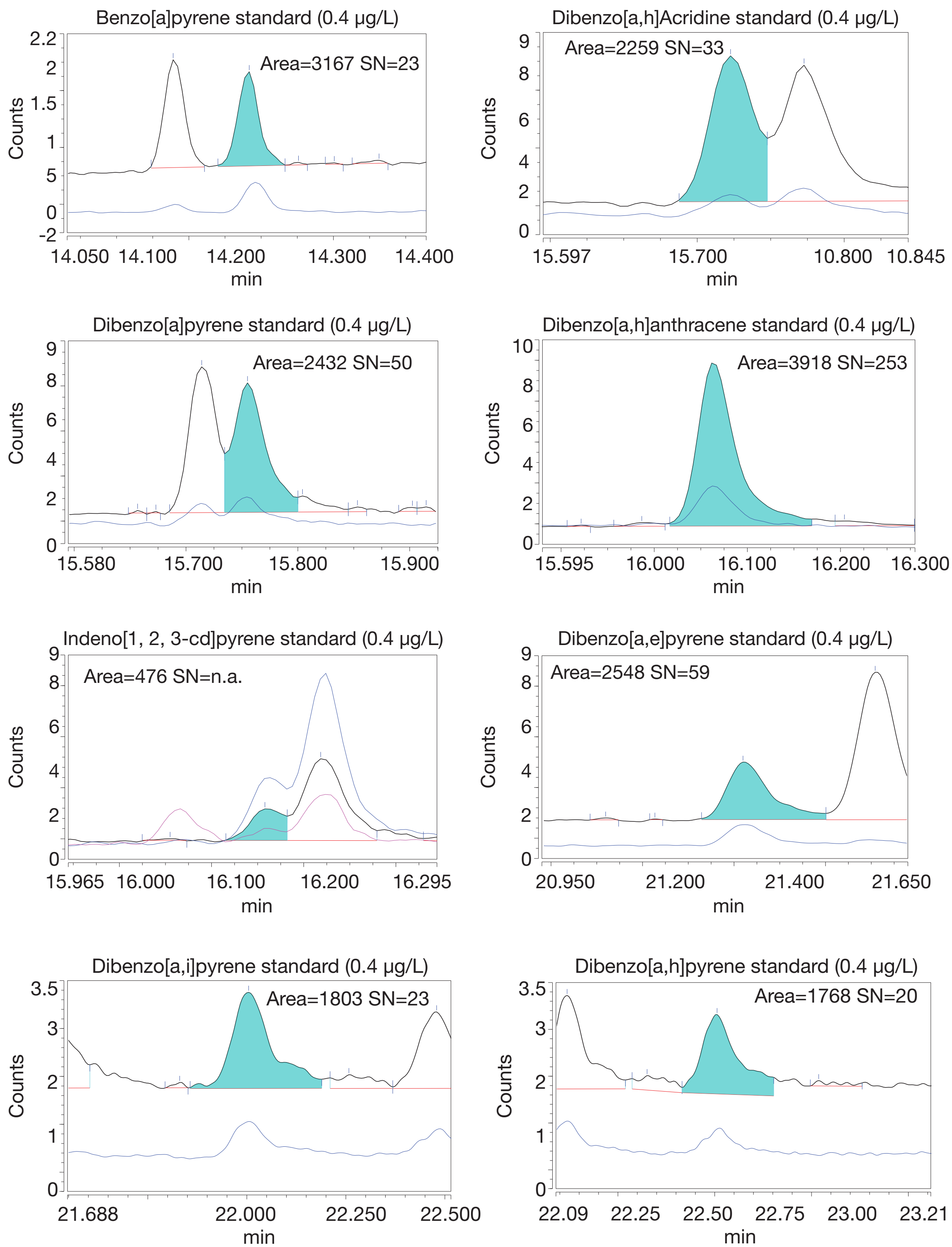


Figure 3. Overlaid SRM (quantifier and qualifier) at 0.4µg/L for critical compound isomers

Resolution

This new method enables the resolution of all critical pairs. Minimum required chromatographic resolution has been also obtained for all isomers (Table 4). Per NF ISO 28540, a minimum of chromatographic resolution of R > 0.8 is required for benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[j]fluoranthene.

Table 4. Chromatographic peak resolution

Peak name	Resolution (SM)
2-Methylnaphthalene 1-Methylnaphthalene	2.7
Phenanthrene Anthracene	1.5
PCB-31 PCB-28	0.8
Benzo[a]fluorene Benzo[b]fluorene	2.2
Benzo[a]anthracene Chrysene	2.3
Benzo[b]fluoranthene Benzo[k]fluoranthene	0.9
Benzo[k]fluoranthene Benzo[j]fluoranthene	1.2
Benzo[e]pyrene Benzo[a]pyrene	1.7
Dibenzo[a,h]acridine Dibenzo[a,j]acridine	0.7
Indeno[1,2,3-cd]pyrene Dibenzo[a,h]anthracene	0.8
Dibenzo[a,e]pyrene Dibenzo[a,i]pyrene	1.1
Dibenzo[a,i]pyrene Dibenzo[a,h]pyrene	1.3

Reproducibility

Appropriate reproducibility results at the LOQ level (0.4 µg/L) were obtained with several consecutive injections of water samples. Each sample has been injected 10 times (from same vial) and the RSD (%) values were calculated using internal standard calibration. All compounds demonstrated excellent reproducibility results and the RSD (%) was less than 25%.

Table 5. Reproducibility at LOQ (0.4µg/L)

Compound	RSD (%)
Naphthalene	8
2-Methylnaphthalene	9
1-Methylnaphthalene	8
Acenaphthylene	12
Acenaphthene	22
Fluorene	15
PCB-18	9
Phenanthrene	9
Anthracene	8
PCB-31	9
PCB-28	10
PCB-52	6
PCB-44	6
PCB-101	5
Fluoranthene	5
PCB-149	5
PCB-118	4
Pyrene	5
PCB-153	4
Benzo[a]fluorene	6
Benzo[b]fluorene	5
PCB-138	6
PCB-180	5
PCB-170	8
Benzo[a]anthracene	8
Chrysene	19
Benzo[b]fluoranthene	6
Benzo[k]fluoranthene	7
Benzo[j]fluoranthene	6
Benzo[e]pyrene	7
Benzo[a]pyrene	8
3-MethylCholanthrene	11
Dibenzo[a,h]acridine	14
Dibenzo[a,j]acridine	17
Indeno[1,2,3-cd]pyrene	17
Dibenzo[a,h]anthracene	14
Benzo[g,h,i]perylene	14
Dibenzo[a,e]pyrene	16
Dibenzo[a,i]pyrene	16
Dibenzo[a,h]pyrene	14

Robustness

Robustness was tested with a QC sample in solvent at 0.4µg/L (LOQ),injected after every 10 matrix samples (wastewater and drinking water). After 80 consecutive injections, the results showed good robustness of the proposed method for all compounds (Figures 4 and 5). All compounds were within the acceptable 2σ of standard deviation.

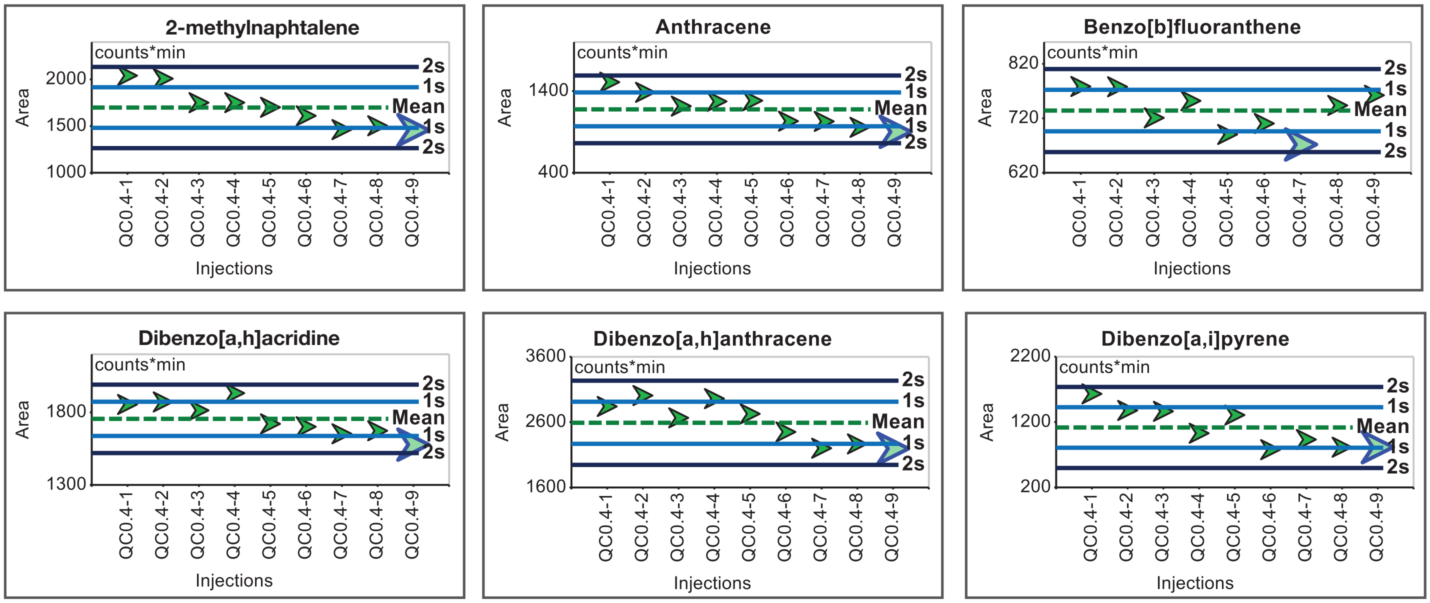


Figure 4. Critical compounds - QC results at 0.4µg/L (within 2σ deviation)

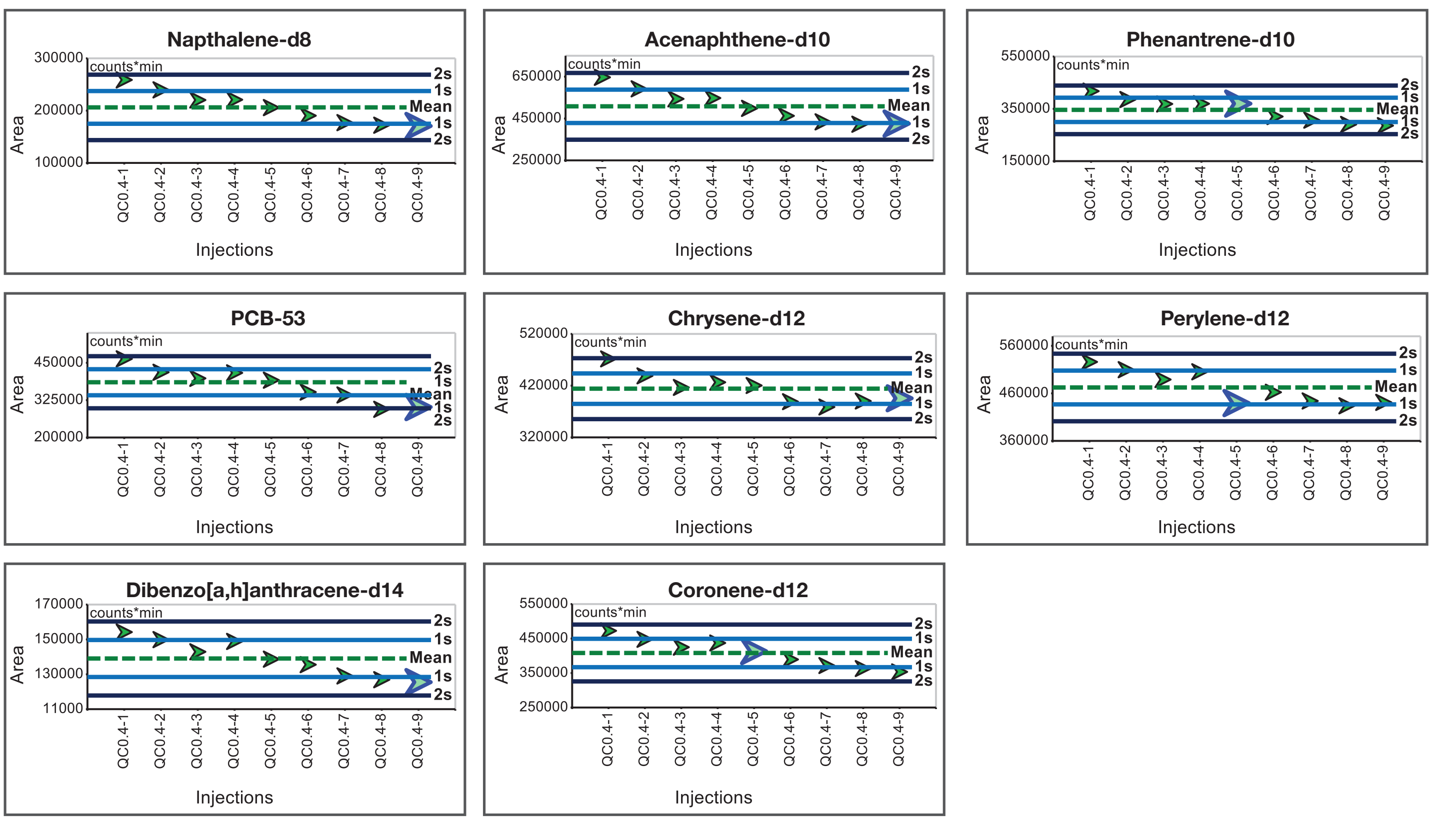


Figure 5. ISTD — QC results (within σ deviation)

Software analysis

Thermo Scientific™ Chromeleon™ 7.3 CDS Software can help laboratories improve data reprocessing and save time. For example, the customized interactive view (Figure 6) makes it easy to quickly check the calibration curve so that the all level response (blue dots) fit within the tolerance limits (red line). Criteria can be adjusted for each calibration level. Interactive charts within the software helps users to perform a quick quality control test. This automated process can be easily adapted to meet laboratory requirements and thereby minimizing the time needed for checking data.

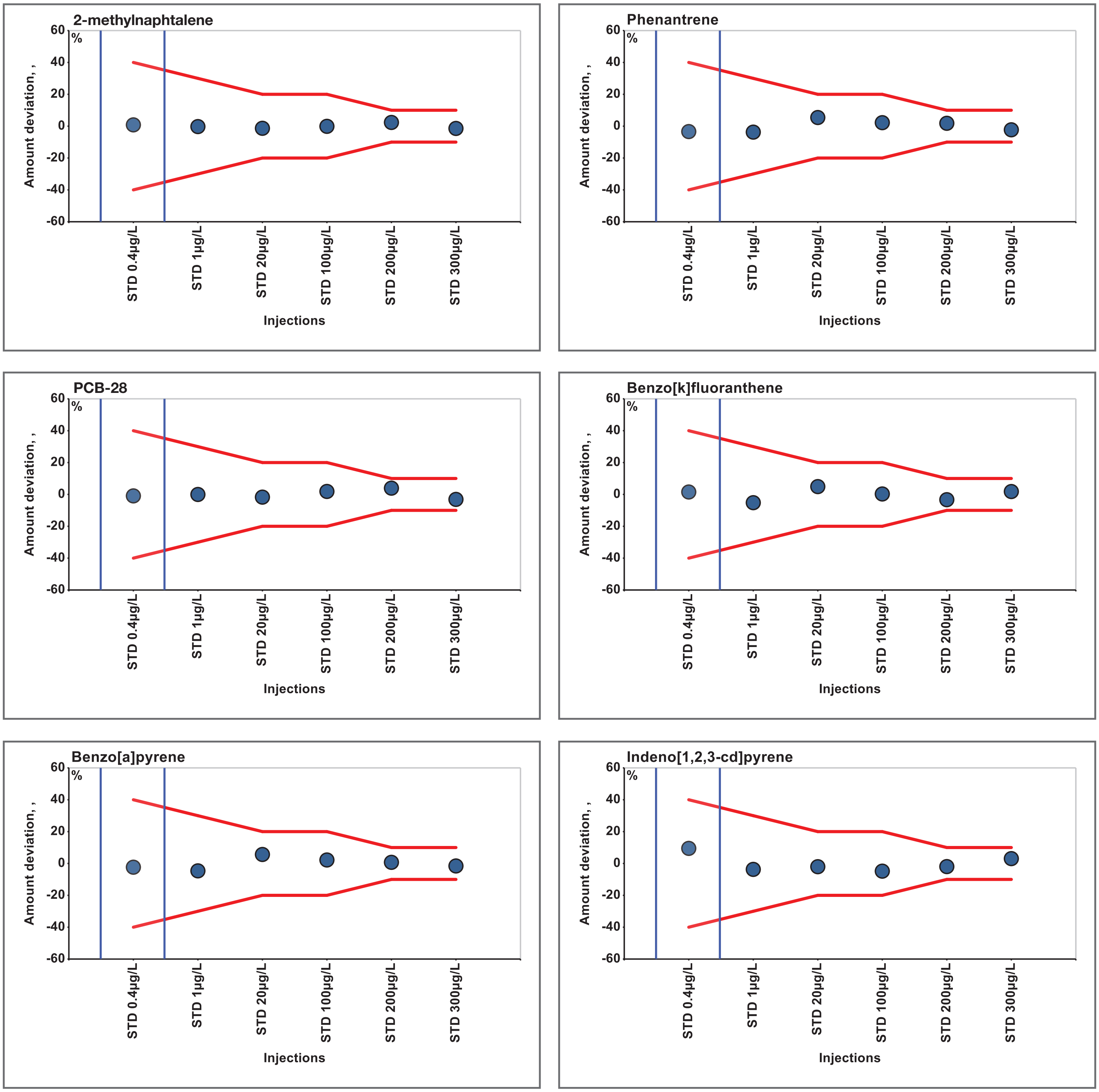


Figure 6. Interactive charts for calibration curve check

Conclusion

This method demonstrates an integrated sample preparation and instrument set-up that improves the PCB and PAH analysis workflow by:

- Incorporating a simplified sample preparation step that reduces sample volume and requires less solvent for extraction
- Implementing an innovative column chemistry for retention and appropriate separation of challenging compounds in the shortest possible time frame (<25 min)
- Using a PTV injector module to analyze a wider compound volatility and chemistry range within the same run.
- Incorporating an AEI source into the TSQ 9000 to achieve the highest sensitivity.
- Utilizing flexible view settings using Chromeleon 7.3 CDS Software to improve data reprocessing and save time

In summary, this new method offers faster turnaround time, improved sensitivity and increased coverage.

Find out more at **thermofisher.com/TSQ9000**