



Analyzing Wastewater Effluents for PAH's and PBDE's Using the Agilent 7000 Triple Quadrupole GC/MS

Application Note

Environmental

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Abstract

An analytical method has been developed on the Agilent 7000 series Triple Quadrupole GC/MS for the analysis of polyaromatic hydrocarbons and polybrominated diphenyl ethers in wastewater. With a single extraction and no cleanup, this method meets the detection limit requirements of the United Kingdom Chemical Investigations Programme.

Introduction

The European Union Water Framework Directive (2000/60/EC) [1] promotes sustainable water use, including the long-term reduction of wastewater contaminant discharges to the aquatic environment. It is supplemented by the Priority Substances Daughter directive (PSDD), which establishes Environmental Quality Standards (EQSs) for priority substances. The EQSs define concentrations of chemical contaminants that are consistent with good chemical status in EU water bodies. A clearer understanding of the occurrence, concentration, and behavior in waste water treatment of these substances is required in order to address the PSDD obligations.

To meet this challenge, UK Water Industry Research (UKWIR), in collaboration with the UK Environment Agency, has created the Chemical Investigations Programme (CIP) for the management and control of concentrations of priority substances. This program includes the quantification of risk and assessment of treatment options through the analysis of crude sewage, process streams, final effluents, and sludge.



Agilent Technologies

The CIP focuses on several categories of priority substances, including polyaromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs). This application note describes the development of a single extraction and sensitive method for the detection of these two classes of priority substances on the Agilent 7890 Series GC System coupled to the 7000 Triple Quadrupole GC/MS to meet the requirements of the CIP. It provides a single method for all 14 analytes, using only one extraction step and minimal or no cleanup, in both µg/L and ng/L concentrations. The reporting limits of the method are all below 3.0 ng/L, and well below the CIP analytical quality control (AQC) requirements.

Experimental

Reagents and Standards

Reagent or Standard	Source
Hexane	HPLC grade, Rathburn Chemicals Ltd, UK
Ammonia solution	35% aqueous solution
Polyaromatic hydrocarbons (PAHs)	QMX Thaxted, UK
Polybrominated diphenyl ethers (PBDEs)	Accustandard, Kinesis, UK
¹³ C internal standards (ISTD)	Sigma Aldrich, UK

Calibration standard solutions were prepared by accurately weighing each analyte into a volumetric flask and diluting with hexane to generate a mixed stock solution. Subsequent calibration and fortification solutions were created by dilution from this stock using hexane. These calibration standards also contained a deuterated and ¹³C-labeled internal standard cocktail.

Instruments

This method was developed on the Agilent 7890A GC with a multimode inlet (MMI) in solvent vent mode and a 4-mm liner packed with glass beads. The GC was coupled to the Agilent 7000B Triple Quadrupole GC/MS. The instrument conditions are listed in Table 1.

Table 1. GC and MS Instrument Conditions

GC run conditions	
Analytical column	Column 1: 30 m × 0.25 mm, 0.25 µm HP-5 5% Phenyl Methyl Siloxan (p/n 19091J-233)
Injection volume	25 µL
Injection mode	MMI in solvent mode, 4-mm liner packed with glass beads
Inlet temperature	60 °C
Vent flow	100 mL/min for 0.09 minutes
Oven temperatures	60 °C for 2 minutes 25 °C/min to 300 °C; hold for 8.4 minutes
Carrier gas	Helium Velocity 30 cm/s constant flow mode
Transfer line temp	300 °C
Run time	20 minutes
MS conditions	
Acquisition parameters	El mode; multiple reaction monitoring (MRM)
Collision gas	Nitrogen, constant flow, 1.5 mL/min
Quench gas	Helium, constant flow, 2.25 mL/min
MS temperatures	Source 300 °C; Quadrupoles 230 °C

Sample Collection, Preparation and Cleanup

Samples were collected in 500-mL amber glass bottles. A 100-mL aliquot of the sample was taken and placed in a 250-mL amber screw cap bottle. A 50-µL amount of 35% aqueous ammonia solution was added by pipette, and the sample diluted with ultrapure water to approximately 200 mL. The internal standard solution was then added, followed by 10 mL of hexane. The vessel was then placed on a bottle roller overnight (a minimum of 12 hours) to extract the analytes into the organic phase. The bottle was topped with ultrapure water.

A pipette was used to take a 5-mL aliquot of the upper, organic hexane phase. This was then concentrated under a flow of nitrogen to 250 µL and transferred to a 2-mL autosampler vial for analysis by GC/MS/MS. The sample extracts were shown to be stable if stored refrigerated and analyzed within 28 days of extraction.

Analysis Parameters

The 7000 Triple Quadrupole GC/MS analysis parameters for the analytes and their internal standards are shown in Tables 2 and 3.

Results and Discussion

Chromatographic Separation

This method resolves eight PAH's and six PBDE's in less than 20 minutes, with the exception of benzo(b)fluoranthene and benzo(k)fluoranthene, which are partially resolved (Figure 1). Combined with the multiple reaction monitoring (MRM) MS detection, this chromatographic approach provides low interference and sensitive detection.

Table 2. MS/MS Analysis Parameters

Compound	Retention time (min)	Precursor ion	Product ion	Collision energy (V)
Naphthalene	6.8	128	127	20
		128	102	22
Anthracene	10.1	178	176	34
		202	201	30
Fluoranthene	11.3	202	200	50
		408	248	22
PBDE 28	11.8	406	246	20
		406	167	25
PBDE 47	12.9	486	326	28
		484	324	32
PBDE 100	13.9	566	406	28
		404	297	35
PBDE 99	14.3	566	406	28
		404	297	35
Benzo(b)Fluoranthene	14.4	252	250	42
		252	248	40
Benzo(k)Fluoranthene	14.4	252	250	42
		252	248	40
Benzo(a)Pyrene	15.0	252	250	42
		252	248	40
PBDE 154	15.4	644	484	20
		484	375	40
		484	324	35
PBDE 153	16.2	644	484	20
		484	324	35
		484	375	40
Indeno(123cd)Pyrene	17.8	276	274	38
Benzo(Ghi)Perylene	18.6	276	274	42

Accuracy of Quantitation

Calibration curves for all of the PAH's and PBDE's spiked into final effluent provide excellent correlation coefficients (>.999) that assure accurate estimations of quantitation for all of the analytes. Representative quantifier ion traces and calibration curves are shown in Figures 2 and 3.

Table 3. Internal Standard Analysis Parameters

Compound	Retention time (min)	Precursor ion	Product ion	Collision energy (V)
Naphthalene-d8	6.6	136	108	25
Anthracene-d10	8.1	188	160	34
Fluoranthene-d10	11.28	212	210	30
		420	260	22
PBDE 28-C13	11.79	418	258	20
		498	338	28
PBDE 47-C13	12.9	496	336	32
		578	418	28
PBDE 100-C13	13.9	416	308	35
		416	308	35
PBDE 99-C13	14.3	578	418	28
		578	418	28
Benzo(K)Fluoranthene-d12	14.37	264	260	42
Benzo(A)Pyrene-d12	15.0	264	260	42
PBDE 154-C13	15.4	496	388	38
		496	336	33
PBDE 153-C13	16.2	496	336	33
		496	388	38
Indeno(123cd)Pyrene-d12	17.05	288	284	42
Benzo(Ghi)Perylene-d12	18.6	288	284	42

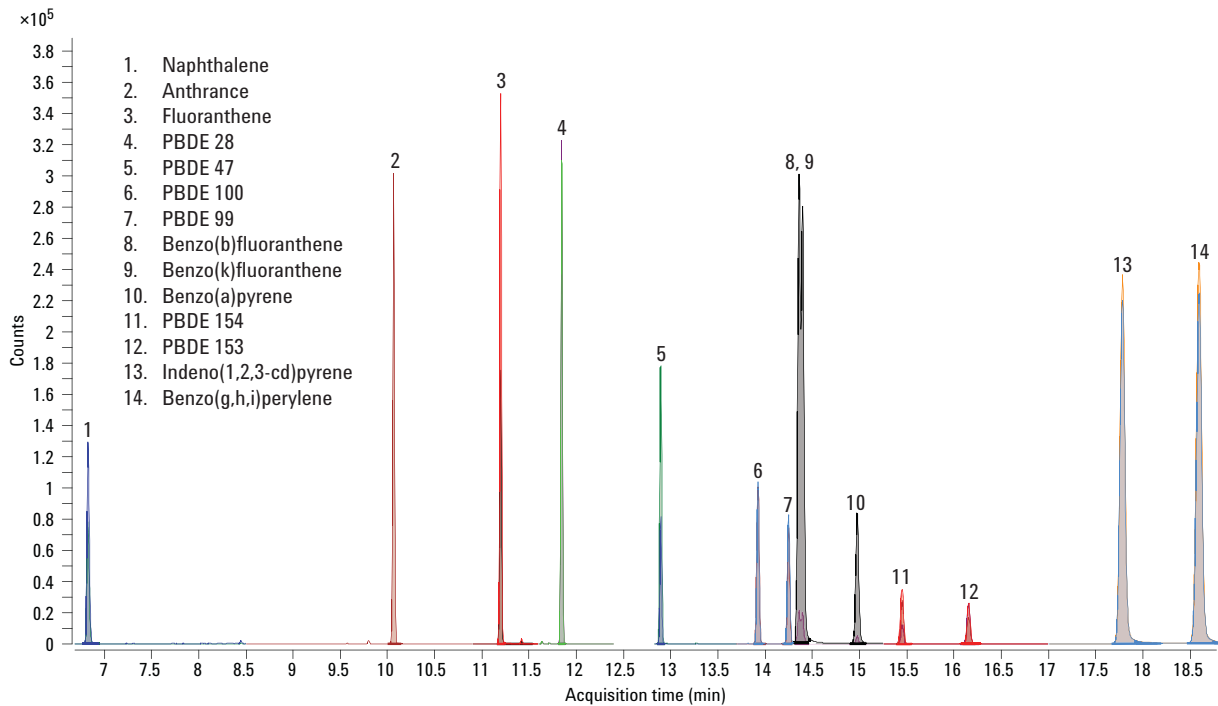


Figure 1. Extracted ion current chromatogram of mid-level calibration standard.

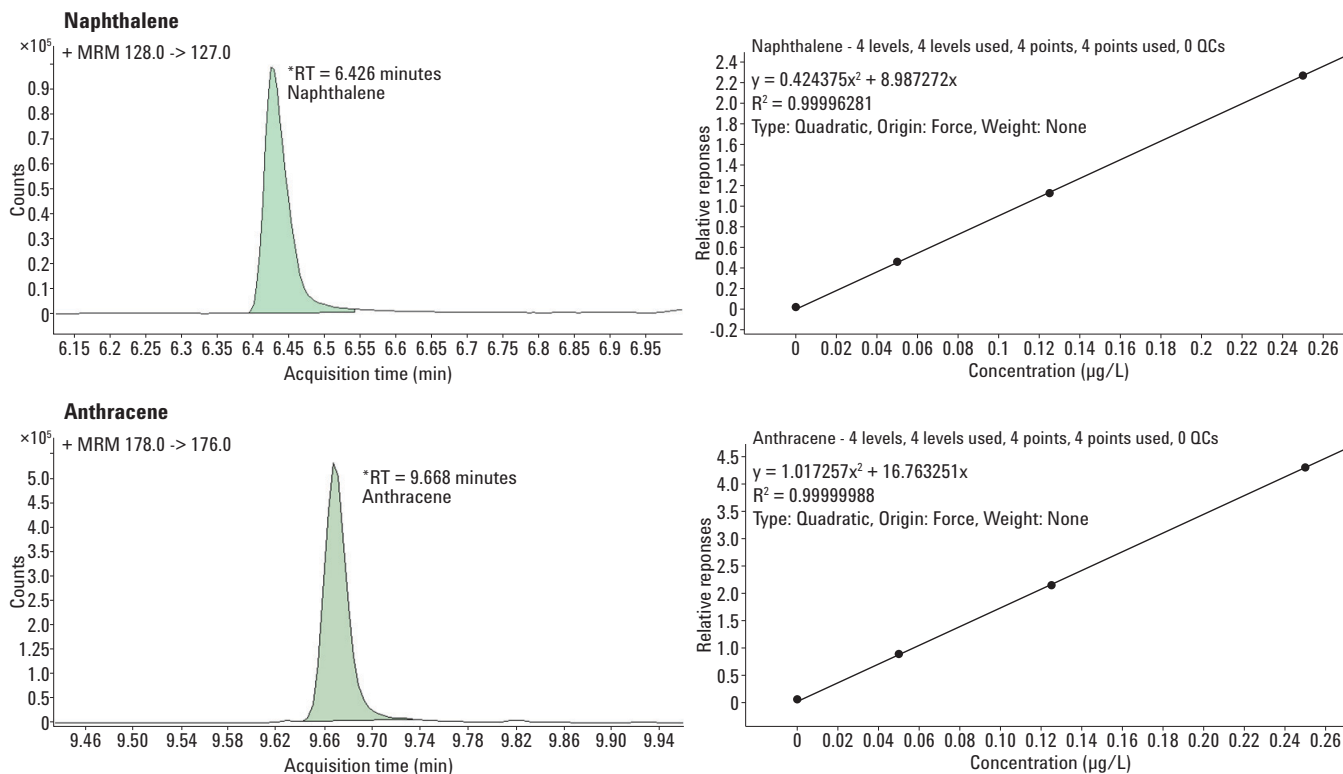


Figure 2. Representative quantifier ion traces and calibration curves for the first seven analytes eluting from the column. (Continued)

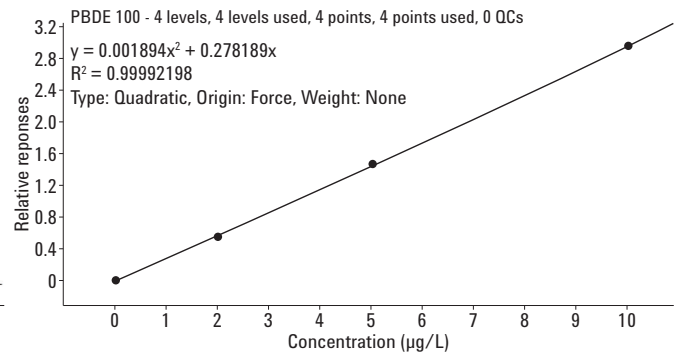
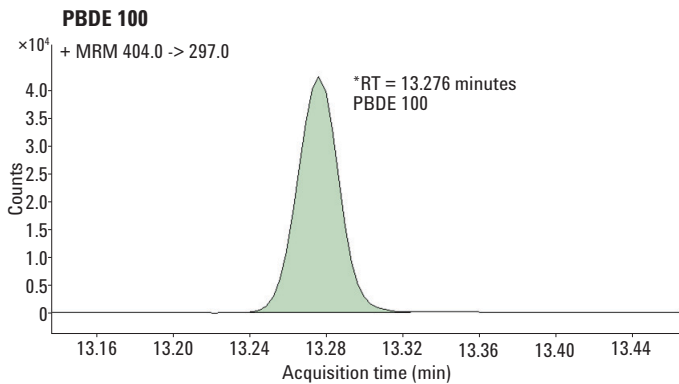
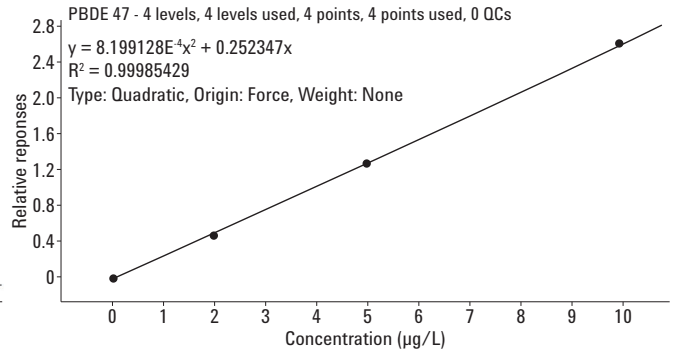
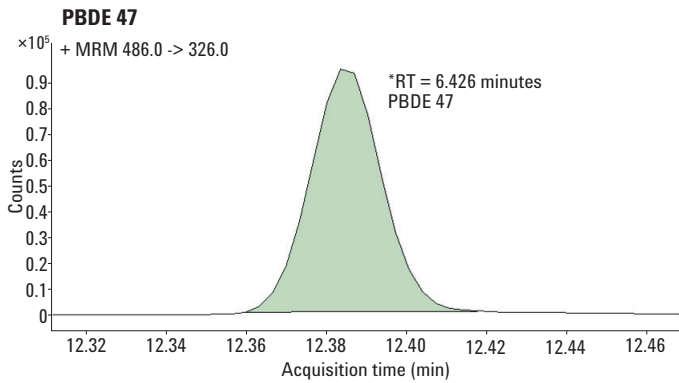
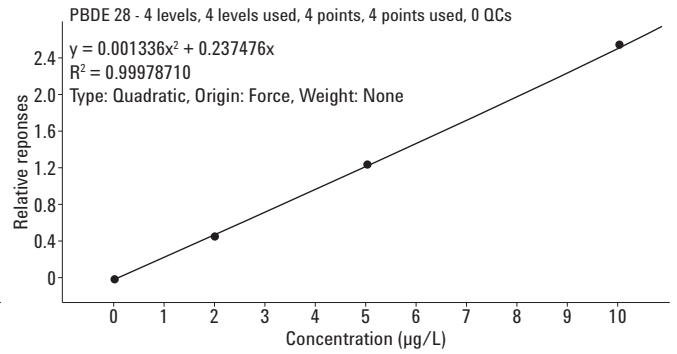
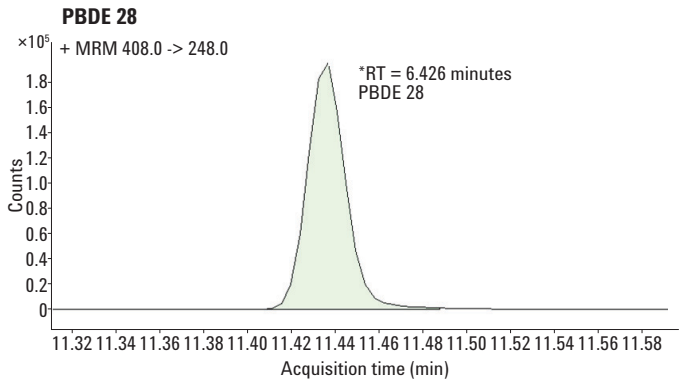
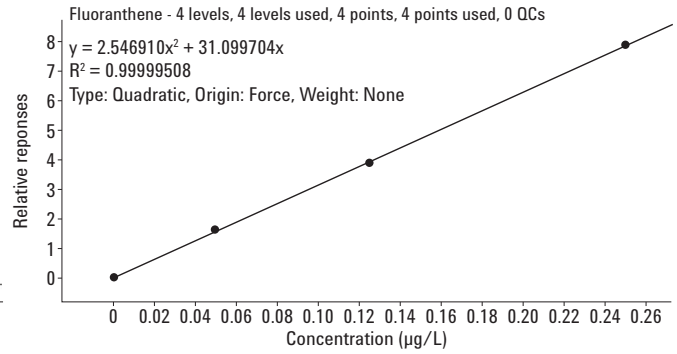
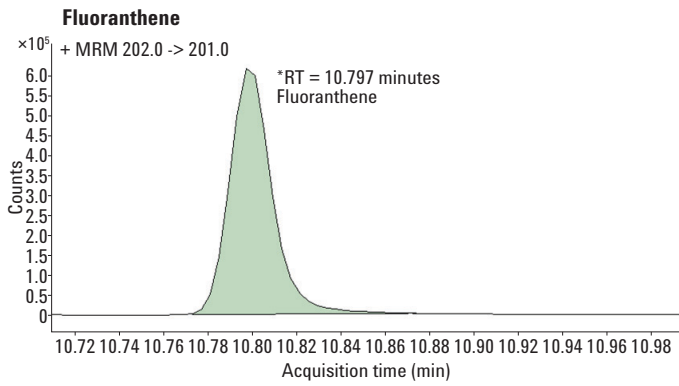


Figure 2. Representative quantifier ion traces and calibration curves for the first seven analytes eluting from the column. (Continued)

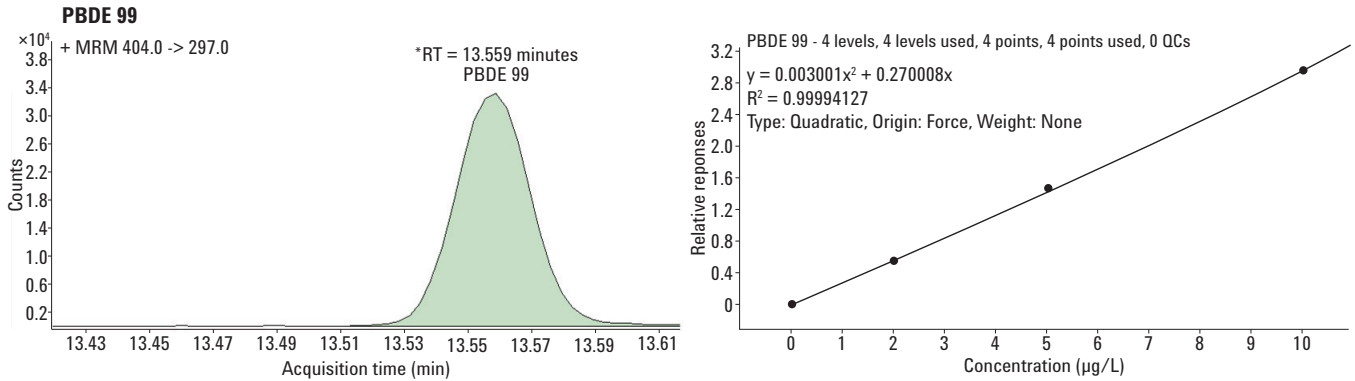


Figure 2. Representative quantifier ion traces and calibration curves for the first seven analytes eluting from the column.

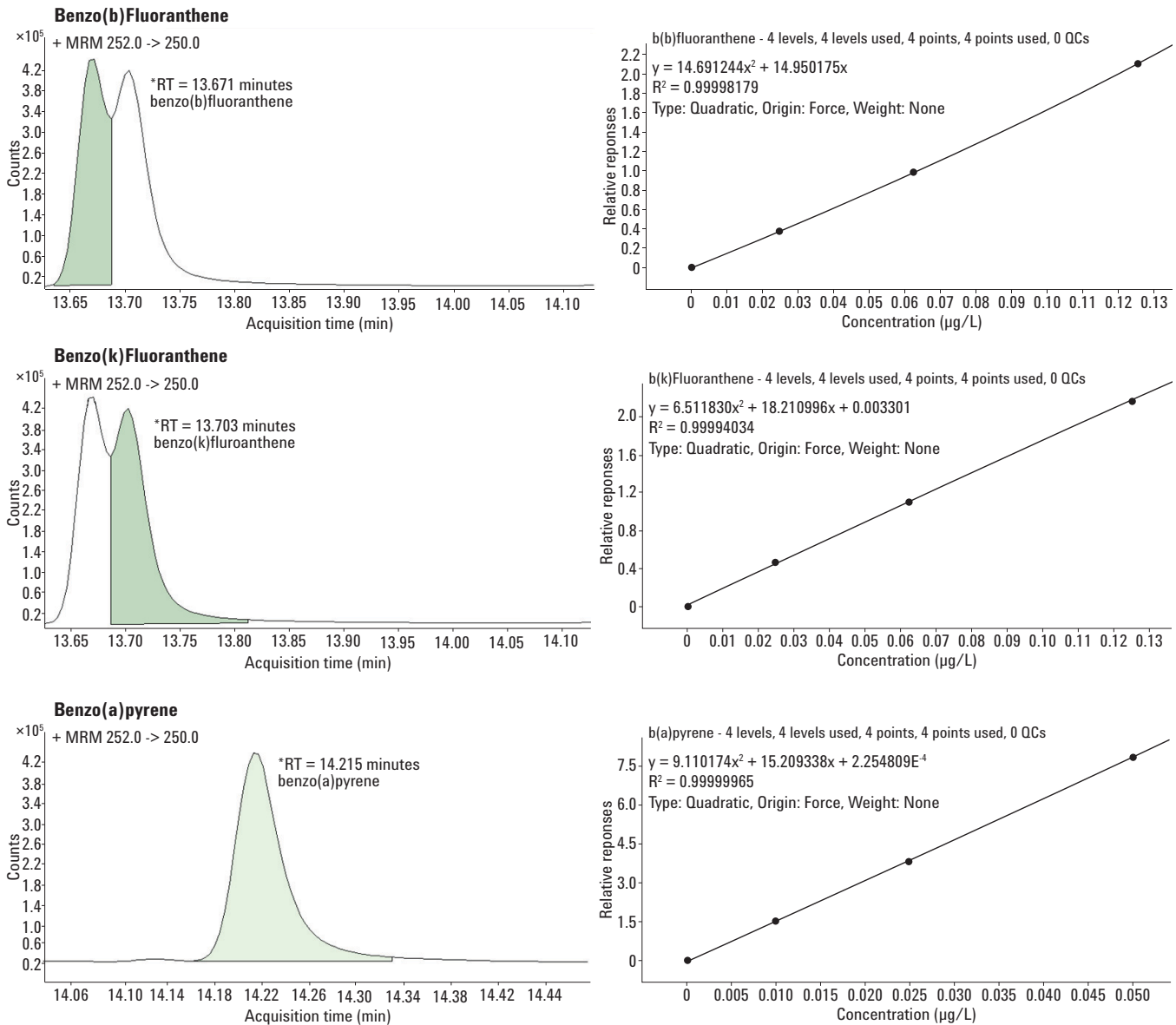


Figure 3. Representative quantifier ion traces and calibration curves for the last seven analytes eluting from the column. (Continued)

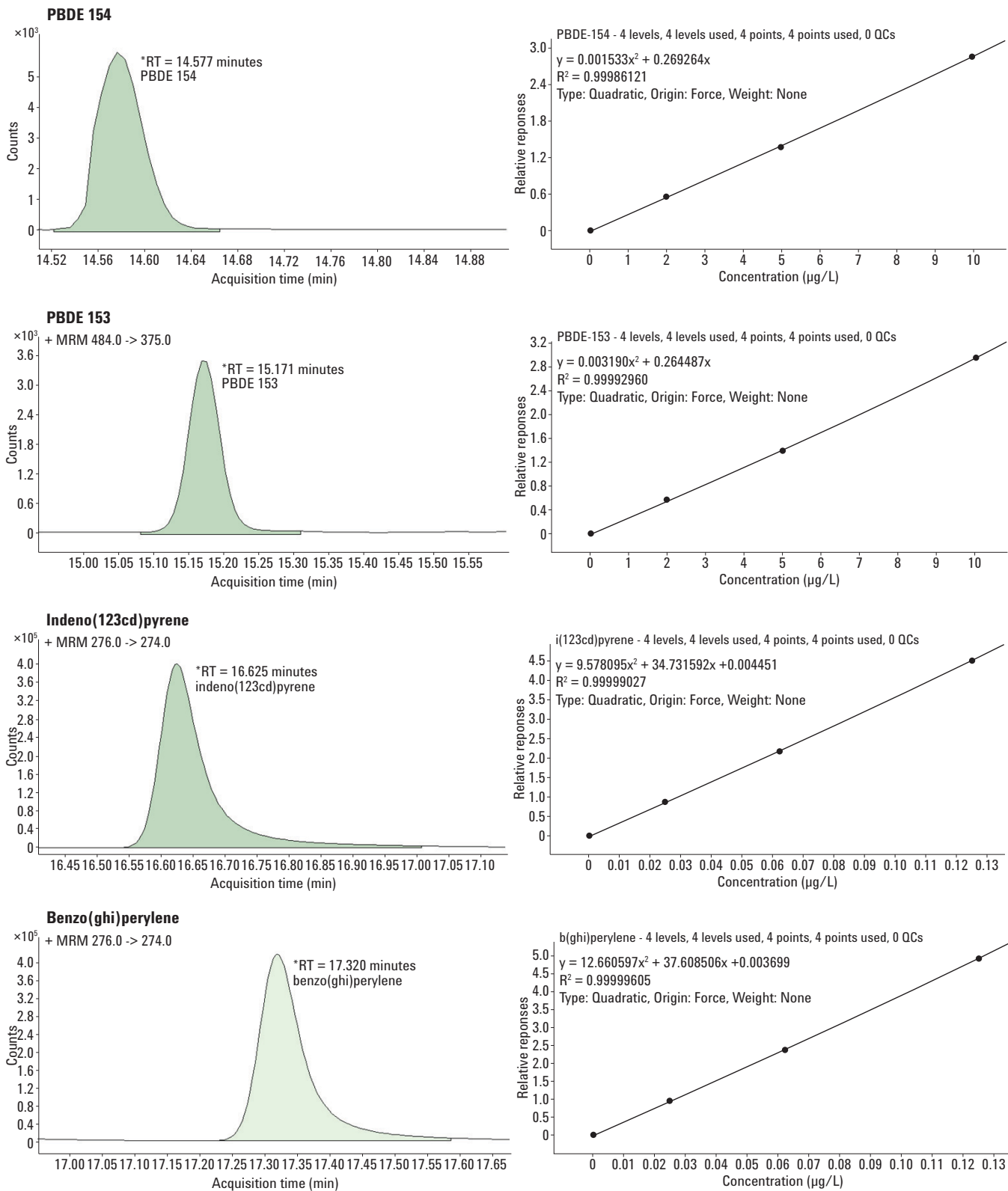


Figure 3. Representative quantifier ion traces and calibration curves for the last seven analytes eluting from the column.

Table 4. CIP Analytical Quality Control (AQC) Limits

Compound	Lowest calibration level	+3 σ	+2 σ	-2 σ	-3 σ	LOD
Naphthalene	0.05 $\mu\text{g/L}$	0.0550	0.0533	0.0467	0.0451	0.001 $\mu\text{g/L}$
Anthracene	0.05 $\mu\text{g/L}$	0.0644	0.0596	0.0404	0.0356	0.002 $\mu\text{g/L}$
Fluoranthene	0.05 $\mu\text{g/L}$	0.0590	0.0560	0.0440	0.0410	0.002 $\mu\text{g/L}$
PBDE 28	2 ng/L	2.4318	2.2887	1.7163	1.5732	0.057 ng/L
PBDE 47	2 ng/L	2.8056	2.5811	1.6831	1.4586	0.185 ng/L
PBDE 100	2 ng/L	2.4544	2.3166	1.7654	1.6276	0.112 ng/L
PBDE 99	2 ng/L	2.5365	2.3865	1.7865	1.6365	0.074 ng/L
Benzo(b)Fluoranthene	0.025 $\mu\text{g/L}$	0.0323	0.0299	0.0201	0.0177	0.003 $\mu\text{g/L}$
Benzo(k)Fluoranthene	0.025 $\mu\text{g/L}$	0.0316	0.0294	0.0206	0.0184	0.002 $\mu\text{g/L}$
Benzo(a)Pyrene	0.010 $\mu\text{g/L}$	0.0114	0.0109	0.0091	0.0087	0.001 $\mu\text{g/L}$
PBDE 154	2 ng/L	2.7789	2.5521	1.6449	1.4181	0.121 ng/L
PBDE 153	2 ng/L	2.8585	2.6103	1.6175	1.3693	0.152 ng/L
Indeno(123cd)Pyrene	0.025 $\mu\text{g/L}$	0.0289	0.0276	0.0224	0.0211	0.001 $\mu\text{g/L}$
Benzo(ghi)Perylene	0.025 $\mu\text{g/L}$	0.0276	0.0267	0.0233	0.0224	0.001 $\mu\text{g/L}$

LOD = Limit of Detection, same as reporting limit in this instance

Limits of Detection and/or Reporting Limit

Table 4 lists the Analytical Quality Control (AQC) limits for each of the analytes. The Limit of Detection or reporting limit in this case varied from 3.0 ng/L for benzo(b) fluoranthene down to 0.06 ng/L for PBDE 28.

Conclusions

The 7000 Triple Quadrupole GC/MS System provided reproducible and sensitive detection of PAHs and PBDEs in wastewater down to levels of less than 3.0 ng/L. This single extraction method with no cleanup and no solvent exchange enables the laboratory to exceed the minimum reporting requirements of the United Kingdom Chemical Investigation Programme.

References

1. Pollutants in Urban Waste Water and Sewage Sludge, http://ec.europa.eu/environment/waste/sludge/pdf/sludge_pollutants_xsum.pdf

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