

# A fast, robust method for routine determination of polycyclic aromatic hydrocarbons (PAH) in drinking water by single quadrupole GC-MS

## Authors

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## Keywords

Polycyclic aromatic hydrocarbons, PAHs, drinking water, GC-MS, single quadrupole, selected ion monitoring, SIM, full scan, FS, ExtractaBrite, electron ionization, EI, fast, robust, routine analysis

## Goal

The aim of this application note is to demonstrate the performance of the Thermo Scientific™ ISQ™ 7000 single quadrupole mass spectrometer, coupled with a Thermo Scientific™ TRACE™ 1310 gas chromatograph, for routine determination of 41 polycyclic aromatic hydrocarbons in drinking water.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic chemicals with two or more benzene rings arranged in various structural configurations resulting in a wide diversity of physical, chemical, and toxicological properties. PAHs are ubiquitous in the environment and originate from incomplete combustion of natural deposits (such as oil, coal, tar, wood, and petroleum) and as a consequence of human activities (such as fuels, vehicle emissions, rubber, plastics, and cigarettes). PAHs are classified as health harming chemicals, potentially as human carcinogens and endocrine disruptors.<sup>1,2</sup> As a consequence, most countries across the world monitor and regulate the presence of PAHs in the environment, food products, and drinking water.<sup>3</sup>

For example, in the United States of America, the Environmental Protection Agency (EPA) added 16 PAHs as priority pollutants with established maximum contaminant level of 0.2 µg/L for benzo[a]pyrene in drinking water.<sup>4</sup> In the European Union (EU), eight PAHs are identified as priority contaminants in water.<sup>5,6</sup>

Analysis of PAHs is usually performed by gas chromatography (GC) coupled with flame ionization detection (FID) or mass spectrometry (MS) or with high-performance liquid chromatography (HPLC) with UV, fluorescence detectors (FLD), or mass spectrometry. One of the main challenges associated with PAH analysis is achieving appropriate quantitative performance and adequate chromatographic resolution for a large number of target compounds without long analysis times, which can limit instrument sample capacity. Although liquid chromatography offers the advantage of shorter run times, the analysis of PAHs is generally carried out using GC as this technique allows greater selectivity, chromatographic resolution, and sensitivity.<sup>7</sup> Non-polar stationary phases (e.g. 5% phenyl methylpolysiloxane) capillary columns are conventionally used for analysis of PAHs as they yield sufficient chromatographic resolution for most of the 16 PAHs listed in the US EPA methods. However, one bottleneck with such columns is that they cannot be operated at high temperatures since this results in peak broadening and tailing for the high boiling compounds, such as benzopyrenes, which can lead to inaccurate quantitation of the compounds. The Thermo Scientific™ TraceGOLD™ TG-PAH capillary columns have been developed to overcome these limitations. A thinner film, the unique bonded chemistry, and the wide temperature range up to 350 °C allow for the resolution of the isobaric compounds and for faster elution of the high boiling point benzopyrenes, ensuring a good peak shape.

In this study, a fast and robust method for the determination of 41 PAHs in drinking water is demonstrated. The TraceGOLD TG-PAH capillary column was tested for chromatographic separation of all the investigated PAHs; whereas selected ion monitoring (SIM) acquisition mode ensured appropriate selectivity and sensitivity when matrix samples were analyzed. Moreover, the Thermo Scientific™ AI/AS 1310 autosampler was used for sample introduction, offering adequate precision and ruggedness for an easy-to-use and cost-effective system configuration for routine laboratory work.

## Experimental

In the experiments described here, an ISQ 7000 single quadrupole mass spectrometer equipped with the ExtractaBrite ion source was coupled to a TRACE 1310 gas chromatograph and a Thermo Scientific™ AI/AS 1310 autosampler. Chromatographic separation was achieved on a TraceGOLD TG-PAH 60 m × 0.25 mm × 0.10 µm column (P/N 26055-0120). Additional GC-MS parameters and a complete list of the target compounds are detailed in Table 1 and Table 2, respectively. The GC oven temperature program was optimized to reduce the analysis time, improve sample throughput, and increase laboratory productivity.

**Table 1. GC-MS operating conditions for PAHs determination in drinking water**

<b>TRACE 1310 GC parameters</b>	
Inlet module and mode	SSL, splitless
Splitless time (min)	1
Septum purge mode, flow (mL/min)	Constant, 5
Carrier gas, carrier mode, flow (mL/min)	He, constant flow, 1.8
<b>Oven temperature program</b>	
Temperature 1 (°C)	80
Hold time (min)	1
Temperature 2 (°C)	210
Rate (°C/min)	45
Temperature 3 (°C)	260
Rate (°C/min)	25
Temperature 4 (°C)	350
Rate (°C/min)	7
Hold time (min)	15
Total GC run time (min)	30
<b>ISQ 7000 Single Quadrupole MS</b>	
Ion source	ExtractaBrite
Transfer line temperature (°C)	350
Source temperature (°C)	350
Ionization mode	EI
Electron energy (eV)	70
Acquisition mode	SIM
<b>Chromatographic column</b>	
TraceGOLD TG-PAH (P/N 26055-0120)	60 m × 0.25 mm × 0.1 µm

**Table 2 (parts 1 and 2). List of target PAH compounds, retention times (RT), SIM quantification and qualifier ions**

Components	RT (min)	Quantifier Ion (m/z)	Qualifier Ion (m/z)
Naphthalene	6.49	128	127
Naphthalene-d <sub>8</sub>	6.49	136	137
Byphenyl	7.13	154	153
Acenaphthylene	7.56	152	151
Acenaphthene	7.64	153	154
Acenaphthene-d <sub>10</sub>	7.64	162	164
Fluorene	8.03	166	165
Dibenzothiophene	8.93	184	139
Phenanthrene	9.05	178	176
Phenanthrene-d <sub>10</sub>	9.05	188	186
Anthracene	9.12	178	176
4H-cyclopenta[def]-phenanthrene	9.81	190	187
Fluoranthene	10.73	202	200
Pyrene	11.25	202	203
Benzo[c]phenanthrene	13.30	228	227
Benzo[ghi]fluoranthene	13.35	226	224
Benzo[a]anthracene	13.77	228	226
Chrysene-d <sub>12</sub>	13.89	240	238
Cyclopenta[cd]pyrene	13.93	226	224
Triphenylene	13.93	228	226
Chrysene	13.97	228	226
Benzo[b]fluoranthene	16.61	252	250
Benzo[k]fluoranthene	16.66	250	250

Components	RT (min)	Quantifier Ion (m/z)	Qualifier Ion (m/z)
Benzo[j]fluoranthene	16.74	252	250
Benzo[a]fluoranthene	16.96	252	250
Benzo[e]pyrene	17.61	252	250
Benzo[a]pyrene	17.76	252	250
Perylene	18.08	252	250
Perylene-d <sub>12</sub>	18.08	264	262
3-methylcolanthrene	18.30	268	252
Dibenzo[a,j]acridine	20.10	279	280
Dibenzo[a,h]acridine	20.20	278	139
Dibenzo[a,j]anthracene	20.26	278	279
Benzo[a,c]anthracene	20.60	278	276
Dibenzo[a,h]anthracene	20.70	278	276
Indeno[1,2,3-cd]pyrene	20.80	276	274
Benzo[b]chrysene	21.05	278	276
Picene	21.23	278	277
Benzo[ghi]perylene	21.75	276	138
7H-Dibenzo[c,g]-carbazole	22.17	267	265
Anthanthrene	22.24	276	137
Dibenzo[b,k]-fluoranthene	25.40	302	150
Dibenzo[a,e]pyrene	27.25	302	303
Coronene	27.70	300	150
Dibenzo[a,h]pyrene	28.23	302	303
Dibenzo[a,i]pyrene	28.75	302	303

### Data acquisition, processing, and reporting

Data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2. Integrated instrument control ensures full automation from instrument set up to data processing, reporting, and storage in compliance with the Title 21 CFR part 11. Simplified e-workflows deliver effective data management ensuring ease of use, sample integrity, and traceability.<sup>8</sup> Chromeleon CDS also offers the option to scale up the entire data handling from a single workstation to an enterprise environment.

### Standard preparation

NIST® SRM® 2260a PAH standard mix at 1–10 µg/mL was purchased from Sigma-Aldrich® (P/N NIST2260A, see Table 6 in Appendix 1 for exact mass concentration). PAH supplement mix for method 8100 at 1000 µg/mL (P/N 31857) and semivolatile (SV) internal standard mix at 2000 µg/mL (P/N 31206) were purchased from Restek®. The PAH standard solutions were combined and then serially diluted in hexane to obtain six calibration standards in the ranges reported in Table 3. The SV internal standard solution was diluted in hexane and added to the calibration standards to obtain a final internal standard concentration of 25 ng/mL. These solvent standards were then used to assess method linearity, instrument detection limit (IDL), and repeatability.

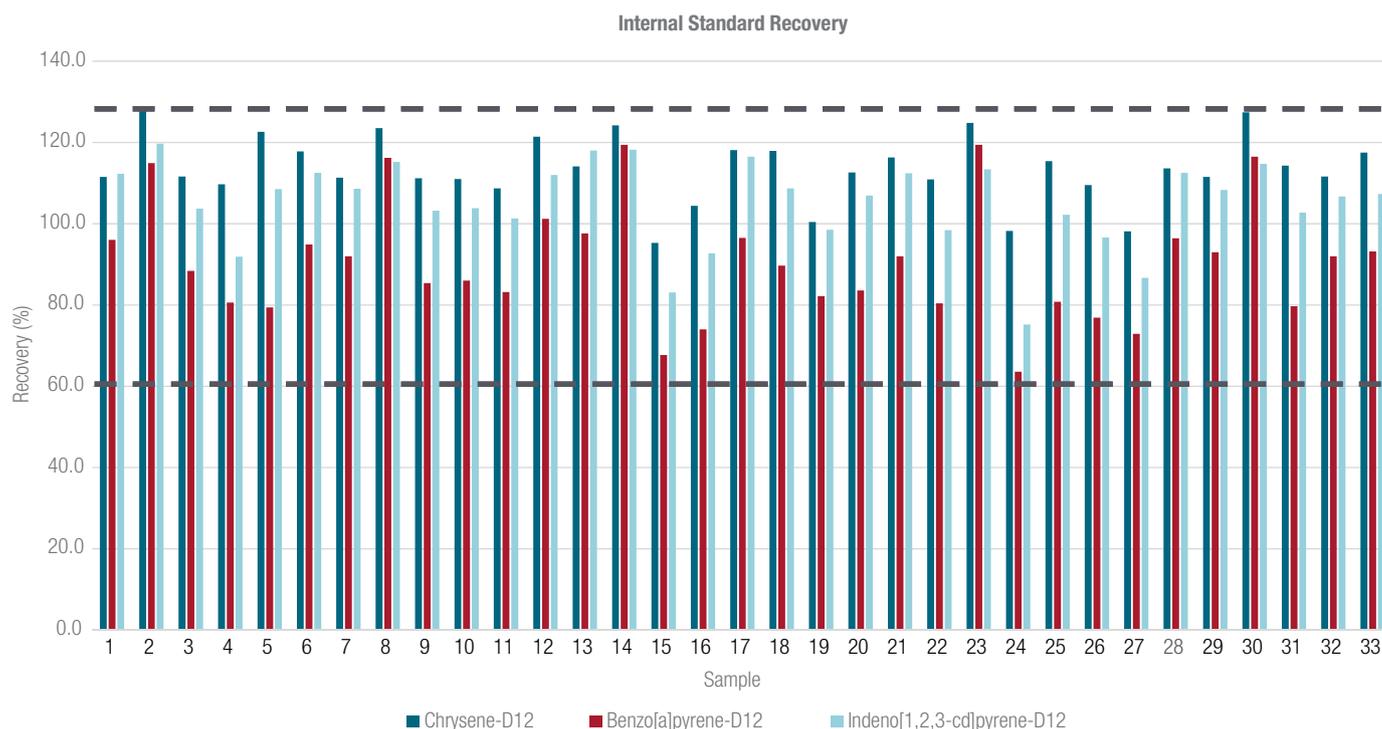
## Sample preparation

Real drinking water samples (n=33) were provided by Laboratorio interno "Francesco Scognamiglio" della società GORI S.p.A, Naples. Samples were extracted using solid phase extraction (SPE) as detailed in the reference analytical methods for water intended for human consumption according to the Italian legislative decree 31/2001.<sup>9</sup> Samples (1000 mL) were spiked with deuterated internal standards (benzo[a]pyrene-d<sub>12</sub> and indeno[1,2,3-cd]pyrene-d<sub>12</sub>) at 100 ng/mL prior to extraction on reversed-phase SPE cartridges previously activated and rinsed with 3 mL of dichloromethane, methanol, and water. The sorbent bed was dried, and analytes were eluted using 5 mL dichloromethane. The extract was then evaporated under nitrogen flow before reconstitution with 500 µL ethylacetate. Chrysene-d<sub>12</sub> was added as syringe standard prior to the analysis at a concentration of 100 ng/mL. The recovery for the internal standards was between 60% and 130% as shown in Figure 1. These samples were analyzed and used to assess instrument robustness over n=100 matrix injections without inlet, column, or ion source maintenance or mass spectrometer tuning.

## Results and discussion

### Chromatographic resolution of isomers

The high selectivity of the TraceGOLD TG-PAH capillary column allowed for the chromatographic separation of the 41 investigated PAHs, ensuring both the resolution of the isobaric compounds listed in the US EPA<sup>10</sup> and EU<sup>11</sup> and regulated priority PAHs and the elution of high boiling dibenzopyrenes in <30 minutes. To demonstrate this, chromatographic resolution was calculated for all targeted compounds (automatically in Chromeleon CDS applying the European Pharmacopoeia formula)<sup>11</sup> with the majority having values  $\geq 1.0$ . The only exception was the critical pairs: triphenylene/chrysene (RT=13.93/13.97 min, respectively) and dibenz[*a,h*]acridine/dibenz[*a,j*]anthracene (RT=20.15/20.26 min, respectively). Co-elution between cyclopenta[*cd*]pyrene and triphenylene was detected at RT=13.93 minutes but these compounds could be easily separated by *m/z*. Moreover, Gaussian peak shape was achieved for the late eluting dibenzo[*a,e*]pyrene, dibenzo[*a,h*]pyrene, and dibenzo[*a,i*]pyrene with peak asymmetry at 5% of the peak height of 1.2, 1.3, and 1.2, respectively. Peak asymmetry was



**Figure 1. Calculated recovery for deuterated internal standards (benzo[a]pyrene-d<sub>12</sub>, indeno[1,2,3-cd]pyrene-d<sub>12</sub>, and chrysene-d<sub>12</sub>).** Samples were spiked with benzo[a]pyrene-d<sub>12</sub> and indeno[1,2,3-cd]pyrene-d<sub>12</sub> at 100 ng/mL prior to extraction on reversed phase SPE cartridges while chrysene-d<sub>12</sub> was added as syringe standard prior to the analysis at a concentration of 100 ng/mL. Recovery was between 60% and 130% for the three deuterated internal standards.

automatically calculated using the CDS applying the EP and USP formula.<sup>11,12</sup> According to this, acceptable peak asymmetry is between 1 (ideal peak) and 1.5; asymmetries >1.5 usually produce imprecise quantitative results. An example of chromatographic separation, data acquired in full scan mode (*m/z* 90–350), is shown in Figure 2 for a solvent standard at 20–200 ng/mL.

### Linearity

Linearity was evaluated by assessing six PAHs concentration levels at the calibration ranges reported in Table 3. Each concentration level was injected in triplicate (n=3). The calculated correlation coefficients ( $R^2$ ) were >0.9986 for all the investigated PAHs with an average value of 0.9992. Moreover, the residual values (measured as % RSD of the average response factors (AvCF)) were <15%, confirming good linear response. The calculated correlation coefficients as well as the average calibration factor % RSDs values are reported in Table 3. Examples of linearity in Chromeleon CDS results browser are shown for benzo[a]pyrene, fluorene, phenanthrene, benzo[b]fluoranthene, and benzo[ghi]perylene in Figure 3 and Figure 4, respectively.

### Instrument detection limit (IDL)

The instrument detection limit reflects the true detection limit of an instrument basing on the precision of a measurement at low analyte levels in solvent based standard.<sup>13</sup> The IDL was determined using Equation 1.

(Equation 1)

$$IDL = t \cdot \text{Amount} \cdot \% \text{RSD}$$

Where:

$t$  = Student's t-value for one-tailed distribution at 99% confidence with 7 degrees (n-1) of freedom corresponding to n=8 injections:  $t=2.998$

Amount = Amount of analyte on column

% RSD = Relative standard deviation of the response

Instrument detection limit was assessed from n=8 consecutive solvent standard injections obtained by serially diluting the NIST SRM 2260a PAH standard

mix to a concentration of 0.5–5ng/mL and the PAH Supplement Mix for Method 8100 to a concentration of 1 ng/mL. IDL was calculated applying Equation 1 and was in the range of 0.3 to 0.9 pg on column as reported in Table 3.

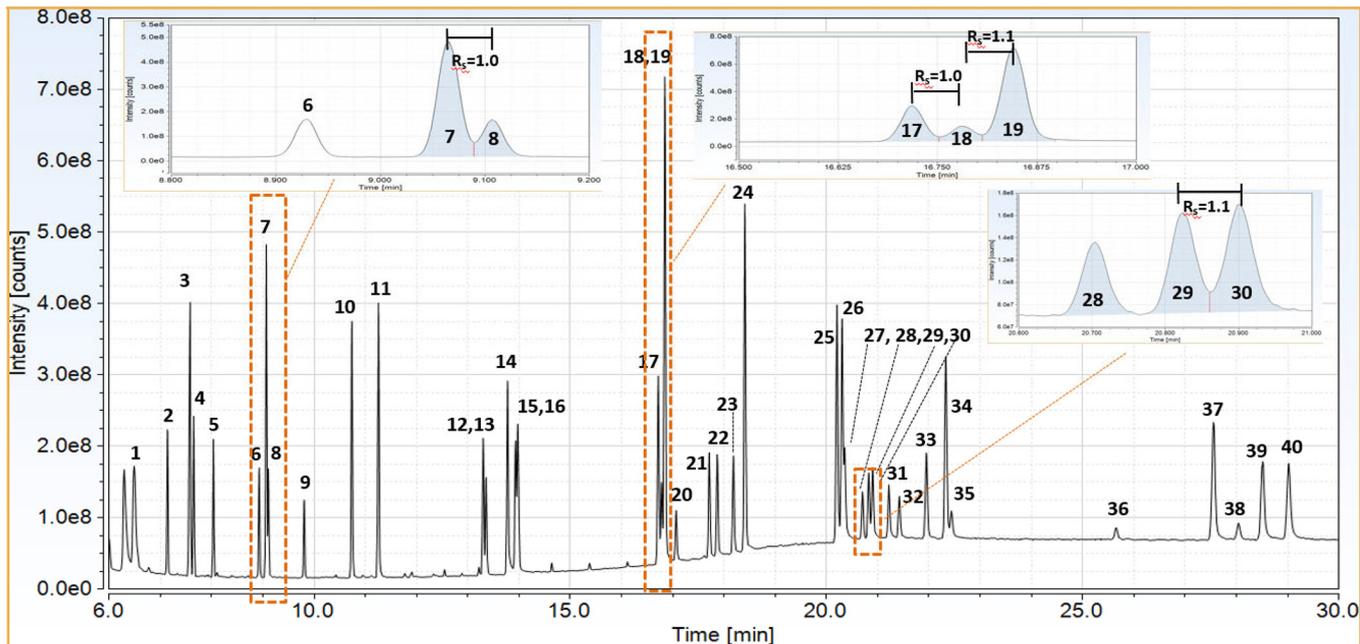
### Repeatability

Repeatability of results was tested by using n=14 consecutive injections corresponding to a concentration of 5–50 ng/mL (NIST SRM 2260a PAH standard mix) and 10 ng/mL (PAH Supplement Mix for Method 8100). The ruggedness of the AI/AS 1310 liquid autosampler combined with the stability of the ExtractaBrite ion source allowed for excellent precision with an average peak area % RSDs <4 and max values of 5.7 as reported in Table 3.

### Quantitation of PAH in drinking water samples

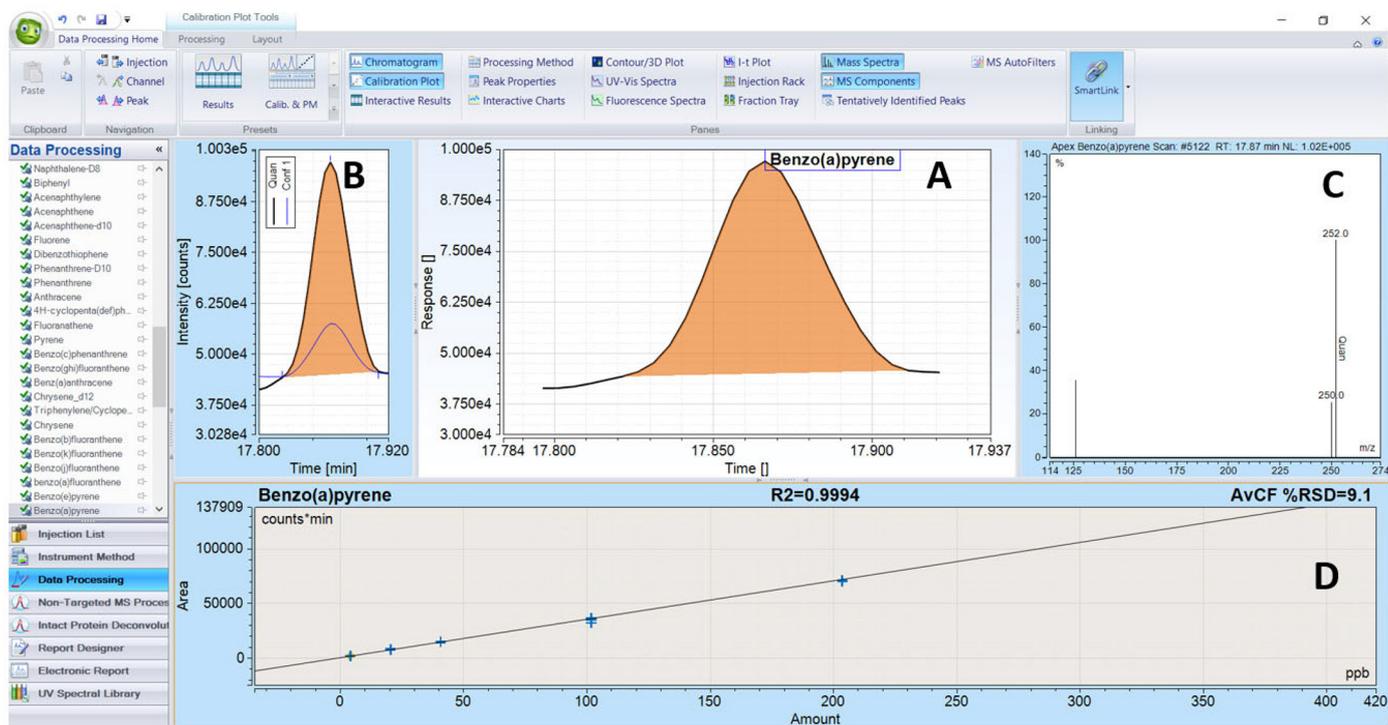
Drinking water samples extracted as detailed in the *Sample preparation* section were analyzed using the conditions reported in Table 1 and Table 2.

Assessment of the unspiked water samples indicated that none of the investigated PAHs exceeded the limits established in the current EU Water Framework Directive for benzo[a]pyrene (0.010 µg/L) and for the sum of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene (0.10 µg/L).<sup>10</sup> In order to ascertain the quantitative performance of the method, n=6 water samples were spiked with the NIST SRM 2260a PAH standard mix at a low (10–100 ng/mL) and high (100–1000 ng/mL) concentration. Since no calibration curve in matrix was available, water samples were blended together and spiked with the standard solutions to obtain a matrix-matched calibration curve in the ranges reported in Table 3. The linearity obtained with the solvent calibration curves was confirmed for the matrix calibration curves with  $R^2$  >0.9980 and average calibration factor % RSDs <15. The average deviation (n=3) of calculated PAHs concentrations for the spiked samples was <13% of the expected concentration for the low spiked concentration and <6% of the expected concentration for the high spiked concentration, as reported in Table 4, confirming the method suitability for the quantitative analysis of PAH in environmental samples.



1=Naphthalene, 2=Biphenyl, 3=Acenaphthylene, 4=Acenaphthene, 5=Fluorene, 6=Dibenzothiophene, 7=Phenanthrene, 8=Anthracene, 9=4H-Cyclopenta[def]phenanthrene, 10=Fluoranthene, 11=Pyrene, 12=Benzo[c]phenanthrene, 13=Benzo[ghi]fluoranthene, 14=Benzo[a]anthracene, 15=Triphenylene/Cyclopenta[cd]pyrene, 16=Chrysene, 17=Benzo[b]fluoranthene, 18=Benzo[k]fluoranthene, 19=Benzo[j]fluoranthene, 20=Benzo[a]fluoranthene, 21=Benzo[e]pyrene, 22=Benzo[a]pyrene, 23=Perylene, 24=3-Methylcholanthrene, 25=Dibenz[a,j]acridine, 26=Dibenz[a,h]acridine, 27=Dibenz[a,j]anthracene, 28=Dibenz[a,c]anthracene, 29=Dibenz[a,h]anthracene, 30=Indeno[1,2,3-cd]pyrene, 31=Benzo[b]chrysene, 32=Benzo[ghi]perylene, 33=7H-Dibenzo[c,g]carbazole, 34=Anthanthrene, 35=Anthanthrene, 36=Dibenzo[b,k]fluoranthene, 37=Dibenzo[a,e]pyrene, 38=Coronene, 39=Dibenzo[a,h]pyrene, 40=Dibenzo[a,i]pyrene

**Figure 2. Chromatographic separation for 41 investigated PAHs in a solvent standard at 20–200 ng/mL acquired in full scan ( $m/z$  90–350).** The TraceGOLD TG-PAH capillary column high selectivity and extended temperature range up to 350 °C allowed for the chromatographic separation of the investigated PAHs in less than 30 minutes. Chromatographic resolution ( $R_s$ ) was  $\geq 1.0$  for all the target compounds with the exception of triphenylene/chrysene ( $RT=13.93/13.97$  min, respectively) and dibenz[*a,h*]acridine/dibenz[*a,j*]anthracene ( $RT=20.15/20.26$  min, respectively). Co-elution between cyclopenta[*cd*]pyrene and triphenylene was detected at  $RT=13.93$  minutes. The extended column temperature range allowed for good peak shape for dibenzo[*a,e*]pyrene, dibenzo[*a,h*]pyrene and dibenzo[*a,i*]pyrene with peak asymmetries  $<1.3$ .



**Figure 3. Chromeleon CDS 7.2 results browser showing benzo[*a*]pyrene SIM quan ion ( $m/z$  252) at the lowest calibration level (4 ng/mL) (A); Overlaid quantifier and confirmation ions (B); SIM mass spectrum (C); calibration curve as well as correlation coefficient ( $R^2$ ) and average calibration factor relative standard deviations (AvCF % RSD) (D). Each calibration level was prepared and analyzed in triplicate ( $n=3$ ).**

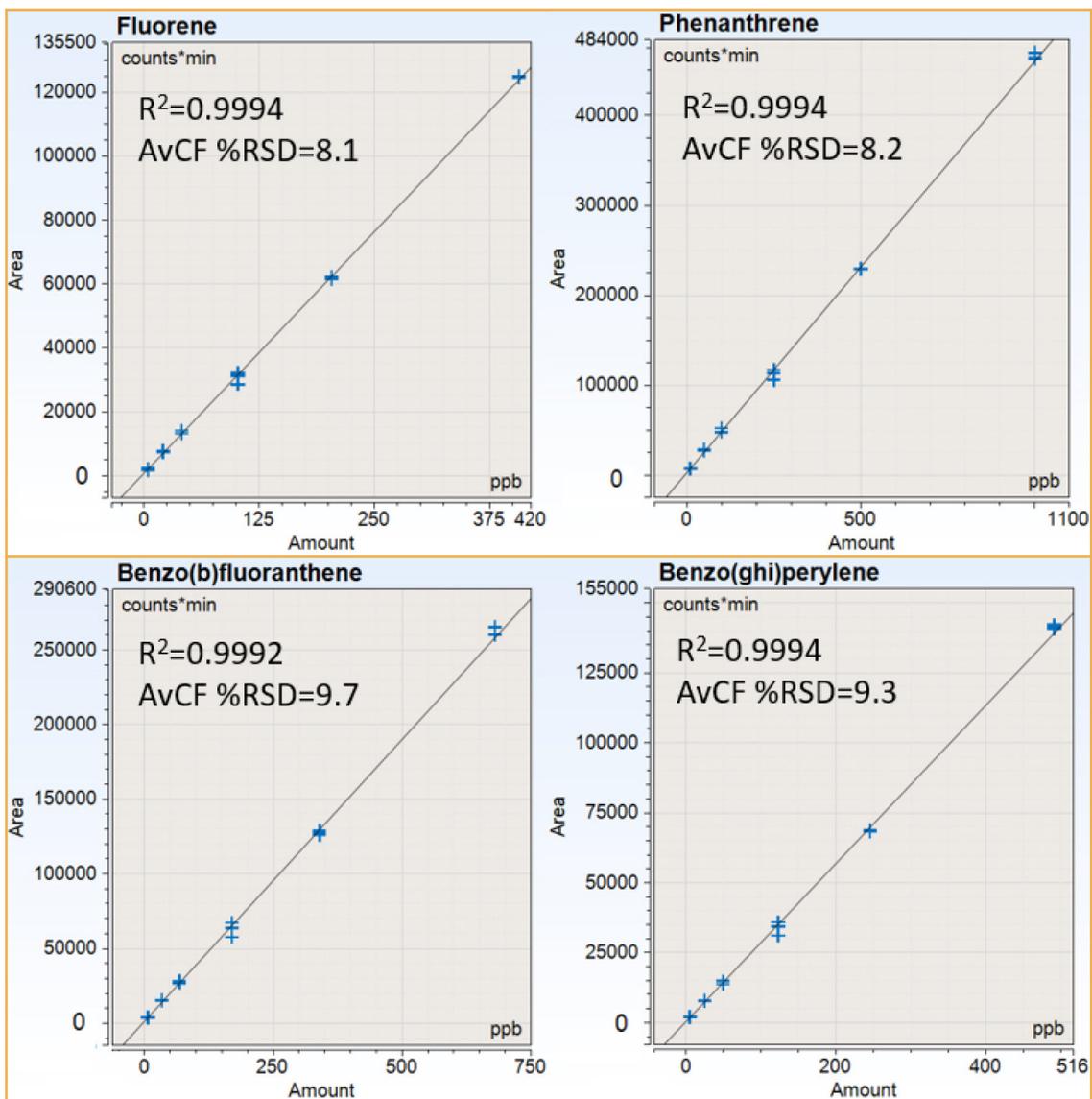


Figure 4. Calibration curves annotated with correlation coefficient ( $R^2$ ) and average calibration factor relative standard deviations (AvCF % RSD) for fluorene, phenanthrene, benzo[b]fluoranthene, and benzo[ghi]perylene. Each calibration level was prepared and analyzed in triplicate ( $n=3$ ).

### Routine analysis of PAHs in drinking water samples

Instrument robustness for routine analysis was evaluated for more than  $n=100$  matrix injections over three days of continuous operation by repeatedly injecting the extracted samples. Moreover, a quality control standard (QC) was spiked at a concentration corresponding to

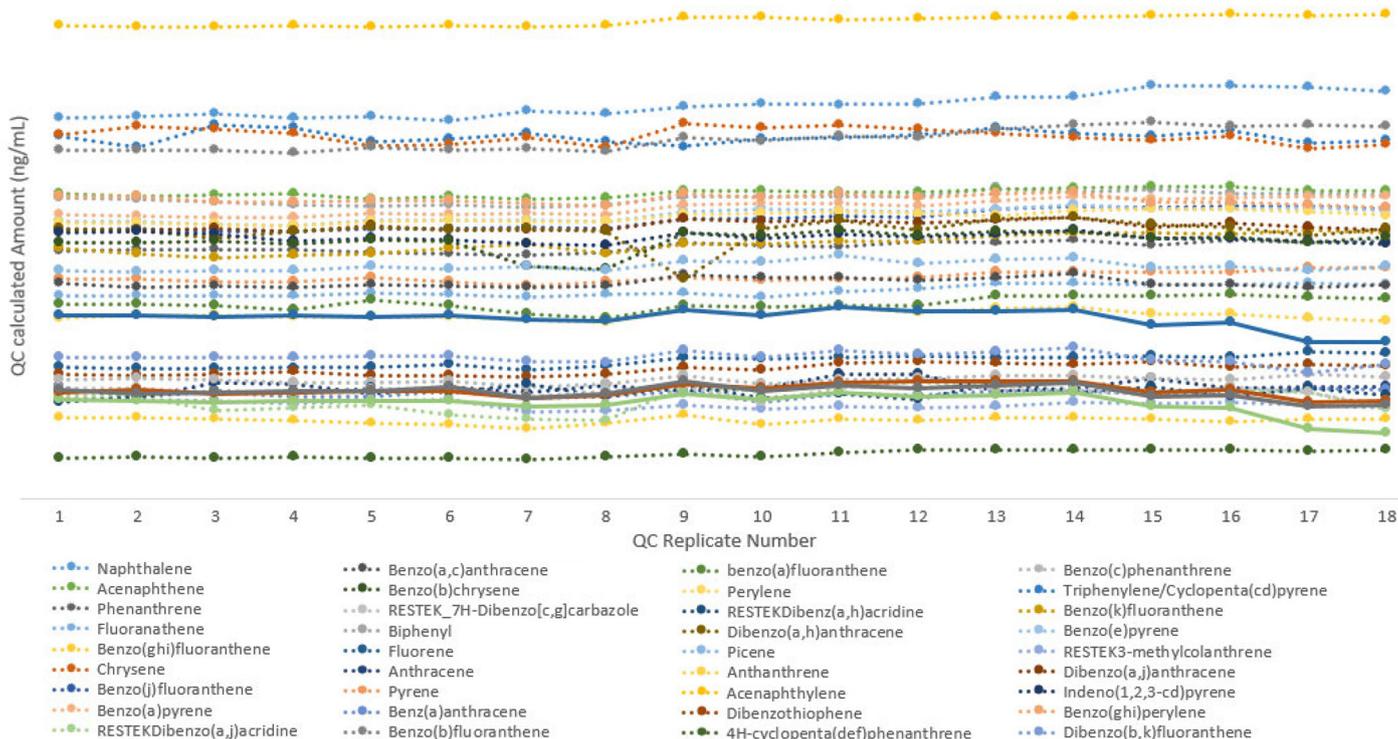
10–100 ng/mL and injected in duplicate every 12 samples to monitor the system stability. Concentration of PAHs present in the QC standard were consistently stable with % RSDs <10 (Figure 5 and Table 5). No column, inlet, or ion source maintenance and no mass spectrometer tuning was performed during the three days continuous sample acquisition, demonstrating a robust system performance critical for routine analysis.

**Table 3. Calibration ranges, calculated correlation coefficients ( $R^2$ ), average calibration factor (AvCF) % RSDs, instrument detection limits (IDLs), and peak area precision (% RSD)**

Components	Calibration range (ng/mL)	Correlation coefficient ( $R^2$ )	AvCF% RSDs	Calculated IDL (pg on column)	% RSD (n=14)
Naphthalene	10–1000	0.9993	8.8	0.8	3.0
Byphenyl	5–500	0.9994	8.5	0.8	3.1
Acenaphthylene	5.5–550	0.9994	8.5	0.7	2.7
Acenaphthene	5–500	0.9994	8.1	0.7	2.9
Fluorene	4–400	0.9994	8.1	0.5	2.7
Dibenzothiophene	4–400	0.9994	8.1	0.3	3.1
Phenanthrene	10–1000	0.9994	8.2	0.6	4.2
Anthracene	3–300	0.9989	11.5	0.5	4.3
4H-cyclopenta[def]phenanthrene	2–200	0.9993	9.1	0.3	2.8
Fluoranthene	7–700	0.9993	8.9	0.7	3.1
Pyrene	7.5–750	0.9993	8.8	0.8	3.3
Benzo[c]phenanthrene	4–400	0.9993	9.0	0.4	2.8
Benzo[ghi]fluoranthene	3–300	0.9993	9.3	0.3	2.1
Benz[a]anthracene	4–400	0.9989	11.3	0.5	3.4
Triphenylene	3.5–350	0.9990	10.3	0.7	3.3
Chrysene	4–400	0.9993	8.9	0.9	3.4
Benzo[b]fluoranthene	7–700	0.9992	9.7	0.8	3.2
Benzo[k]fluoranthene	3–300	0.9991	10.6	0.5	3.6
Benzo[j]fluoranthene	3.5–350	0.9995	7.5	0.5	3.9
Benzo[a]fluoranthene	2–200	0.9992	9.6	0.4	3.6
Benzo[e]pyrene	4–400	0.9993	9.2	0.6	2.6
Benzo[a]pyrene	4–400	0.9994	9.1	0.7	2.6
Perylene	4–400	0.9991	10.7	0.9	3.9
3-methylcolanthrene	5–200	1.0000	6.4	0.7	5.5
Dibenzo[a,j]acridine	5–200	0.9990	9.5	0.8	3.2
Dibenzo[a,h]acridine	5–200	0.9990	4.8	0.6	4.7
Dibenzo[a,j]anthracene	20–400	0.9990	7.4	0.7	4.0
Benzo[a,c]anthracene	2.5–250	0.9990	9.6	0.8	5.1
Dibenzo[a,h]anthracene	20–400	0.9987	10.9	0.7	4.8
Indeno[1,2,3-cd]pyrene	4–400	0.9990	11.6	0.8	4.0
Benzo[b]chrysene	18–360	0.9980	12.8	0.9	4.5
Picene	3–300	0.9987	11.3	0.5	4.5
Benzo[ghi]perylene	14–500	0.9994	9.3	0.6	3.5
7H-Dibenzo[c,g]carbazole	5–200	1.0000	4.7	0.9	5.7
Anthanthrene	10–200	0.9988	10.0	0.4	4.0
Dibenzo[b,k]fluoranthene	7–140	0.9986	11.2	0.4	5.5
Dibenzo[a,e]pyrene	5–200	0.9990	7.0	0.8	4.5
Coronene	10–200	0.9991	8.5	0.7	5.2
Dibenzo[a,h]pyrene	5–200	0.9990	6.7	0.5	5.3
Dibenzo[a,i]pyrene	5–200	0.9990	7.5	0.8	4.7

**Table 4. Quantitation of PAHs spiked in six water samples at low (10–100 ng/mL) and high (100–1000 ng/mL) concentrations.** The average deviation (n=3) of calculated PAHs concentrations for the spiked samples was <13% of the expected concentration for the low spiked concentration and <6% the expected concentration for the high spiked concentration confirming the system suitability for the quantitative analysis of PAH in environmental samples.

NIST SRM 2260a PAH components	Spiked conc. (ng/mL)	Calculated concentrations (ng/mL)			Conc. deviation (% ,n=3)	Spiked conc. (ng/mL)	Calculated concentrations (ng/mL)			Conc. deviation (% ,n=3)
		Sample 1	Sample 2	Sample 3			Sample 4	Sample 5	Sample 6	
Naphthalene	99	92	95	96	3.4	990	993	966	951	2.2
Byphenyl	50	44	46	45	7.4	500	471	467	481	1.6
Acenaphthylene	55	51	50	52	5.3	550	537	527	536	1.0
Acenaphthene	50	46	46	46	5.9	500	483	468	468	1.9
Fluorene	40	38	39	39	2.4	400	400	395	401	0.8
Dibenzothiophene	40	36	36	36	7.4	400	382	366	368	2.3
Phenanthrene	100	95	96	97	2.9	1000	984	956	971	0.7
Anthracene	30	32	31	30	2.3	300	335	301	320	5.3
4H-cyclopenta[def]-phenanthrene	20	19	19	20	2.4	200	197	192	197	1.4
Fluoranthene	70	68	68	70	1.4	700	717	697	695	1.8
Pyrene	80	73	74	74	5.8	800	772	748	749	1.8
Benzo[c]phenanthrene	40	38	38	38	3.6	400	396	386	387	1.3
Benzo[ghi]fluoranthene	30	27	28	28	5.7	300	296	284	292	2.1
Benzo[a]anthracene	40	36	38	36	6.1	400	384	375	367	2.3
Triphenylene	36	36	34	33	3.4	360	355	359	336	3.4
Chrysene	40	36	38	39	4.2	400	340	381	396	2.6
Benzo[b]fluoranthene	70	64	63	64	6.7	700	684	664	662	1.9
Benzo[k]fluoranthene	30	29	28	28	4.0	300	296	289	295	1.2
Benzo[j]fluoranthene	40	33	33	34	12.9	400	356	350	352	1.1
Benzo[a]fluoranthene	20	19	17	17	8.8	200	195	196	196	0.2
Benzo[e]pyrene	40	37	37	37	5.5	400	395	385	382	1.8
Benzo[a]pyrene	40	38	37	38	4.2	400	411	399	400	1.7
Perylene	40	35	36	35	8.8	400	387	379	378	1.3
Dibenzo[a,j]anthracene	40	36	37	37	6.1	400	401	387	383	2.4
Benzo[a,c]anthracene	25	24	24	24	2.9	250	255	246	244	2.1
Dibenzo[a,h]anthracene	40	35	35	36	8.8	400	404	395	394	1.5
Indeno[1,2,3-cd]-pyrene	40	36	36	36	7.4	400	383	349	375	1.5
Benzo[b]chrysene	35	34	33	33	3.4	350	361	349	348	2.1
Picene	30	27	26	27	8.3	300	288	276	278	2.3
Benzo[ghi]perylene	50	47	46	46	5.4	500	492	482	476	1.7
Anthanthrene	20	18	18	17	8.8	200	195	190	187	2.1
Dibenzo[b,k]-fluoranthene	14	13	13	13	5.2	140	143	141	140	1.3
Dibenzo[a,e]pyrene	19	18	17	17	6.5	190	193	189	186	1.9
Coronene	19	18	18	18	3.8	190	196	192	190	1.6



**Figure 5. System stability evaluated over n=100 matrix injections obtained over three days of unattended operations.** A QC was spiked at a concentration corresponding at a calibration level of 10–100 ng/mL and injected in duplicate after every 12 samples. % RSDs of the QC calculated PAHs amount (internal standard correction was applied) was <10% for all PAHs.

**Table 5 (parts 1 and 2). System stability demonstrated by the % RSDs of the QC for calculated concentration of target PAHs with % RSDs <10 over n=18 QC injections corresponding to three days continuous operation.** No column, inlet, or ion source maintenance and no mass spectrometer tuning was performed during the sample acquisition.

Components	QC amount % RSD (n=18)
Naphthalene	9.5
Byphenyl	4.6
Acenaphthylene	3.9
Acenaphthene	3.1
Fluorene	4.7
Dibenzothiophene	4.3
Phenanthrene	4.1
Anthracene	4.9
4H-cyclopenta[def]phenanthrene	3.0
Fluoranthene	4.2
Pyrene	4.2
Benzo[c]phenanthrene	2.7
Benzo[ghi]fluoranthene	2.6
Benz[a]anthracene	2.7
Triphenylene	5.0
Chrysene	6.2
Benzo[b]fluoranthene	8.8
Benzo[k]fluoranthene	7.2
Benzo[j]fluoranthene	7.8
Benzo[a]fluoranthene	5.1

Components	QC amount % RSD (n=18)
Benzo[e]pyrene	5.3
Benzo[a]pyrene	6.3
Perylene	4.4
3-methylcolanthrene	3.2
Dibenzo[a,i]acridine	9.7
Dibenzo[a,h]acridine	4.3
Dibenzo[a,j]anthracene	3.7
Benzo[a,c]anthracene	3.6
Dibenzo[a,h]anthracene	9.1
Indeno[1,2,3-cd]pyrene	3.5
Benzo[b]chrysene	7.7
Picene	4.0
Benzo[ghi]perylene	3.7
7H-Dibenzo[c,g]carbazole	4.4
Anthanthrene	3.6
Dibenzo[b,k]fluoranthene	4.7
Dibenzo[a,e]pyrene	8.1
Coronene	7.4
Dibenzo[a,h]pyrene	5.1
Dibenzo[a,i]pyrene	5.3

## Conclusions

The results obtained in the experiments performed demonstrate that the ISQ 7000 mass spectrometer in combination with the TRACE 1310 GC and the AI/AS 1300 autosampler delivers excellent analytical performance for routine PAHs analysis in drinking water samples.

- Acceptable chromatographic resolution of the critical isomers was achieved in <30 minutes with the high selectivity and extended temperature range up to 350 °C of the TraceGOLD PAH column, allowing for high sample throughput analysis.
- Excellent linearity with correlation coefficient  $R^2 > 0.9980$  and AvCF % RSDs <15 was obtained in solvent standards and in spiked matrix for all analytes over a concentration range of 1 to 1000 ng/mL.
- Low detection limits were obtained with calculated IDL ranging from 0.3 to 0.9 pg on column.
- The high reproducibility and ruggedness of the AI/AS 1310 liquid autosampler allowed for excellent precision with peak area % RSDs <6 for n=14 repeated injections.
- The PAH concentration in all drinking water samples was below the limits established by the current EU regulation; therefore, a quantitative assessment was simulated spiking the samples with standard solution at low and high concentration. The calculated concentrations were  $\pm 13\%$  of the expected amount, confirming system reliability for quantitative analysis.
- More than n=100 matrix samples, including QC samples, were injected over three days of unattended operation to demonstrate consistency of quantitative results, with deviation of calculated concentrations for target compounds <10%. Moreover, no inlet, column, ion source maintenance or mass spectrometer tuning was performed during the sample acquisition.

Overall these data show that the ISQ 7000 single quadrupole mass spectrometer equipped with Extractabrite ion source combined with the AI/AS 1310 liquid autosampler and the Trace 1310 GC represents a cost effective, robust analytical tool for environmental laboratories providing outstanding routine performance for PAH analysis in drinking water samples.

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## Appendix

Table 6 (parts 1 and 2). List of target PAH compounds and mass concentration ( $\mu\text{g/mL}$ ) for NIST SRM 2260a PAH standard mix

NIST SRM 2260a PAH components	Mass Concentration ( $\mu\text{g/mL}$ )
Naphthalene	9.9
Byphenyl	4.8
Acenaphthylene	5.4
Acenaphthene	4.8
Fluorene	4.1
Dibenzothiophene	3.8
Phenanthrene	10.0
Anthracene	3.2
4H-cyclopenta[def]phenanthrene	2.0
Fluoranthene	7.2
Pyrene	7.7
Benzo[c]phenanthrene	3.9
Benzo[ghi]fluoranthene	2.9
Benz[a]anthracene	3.8
Cyclopenta[cd]pyrene	1.7
Triphenylene	3.6
Chrysene	4.0

NIST SRM 2260a PAH components	Mass Concentration ( $\mu\text{g/mL}$ )
Benzo[a]fluoranthene	1.9
Benzo[b]fluoranthene	6.8
Benzo[k]fluoranthene	2.9
Benzo[j]fluoranthene	3.6
Benzo[e]pyrene	3.9
Benzo[a]pyrene	4.1
Perylene	3.8
Dibenzo[a,j]anthracene	3.9
Benzo[a,c]anthracene	2.5
Dibenzo[a,h]anthracene	3.9
Indeno[1,2,3-cd]pyrene	3.8
Benzo[b]chrysene	3.5
Picene	2.8
Benzo[ghi]perylene	4.9
Anthanthrene	1.9
Dibenzo[b,k]fluoranthene	1.4
Dibenzo[a,e]pyrene	1.9
Coronene	1.9

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