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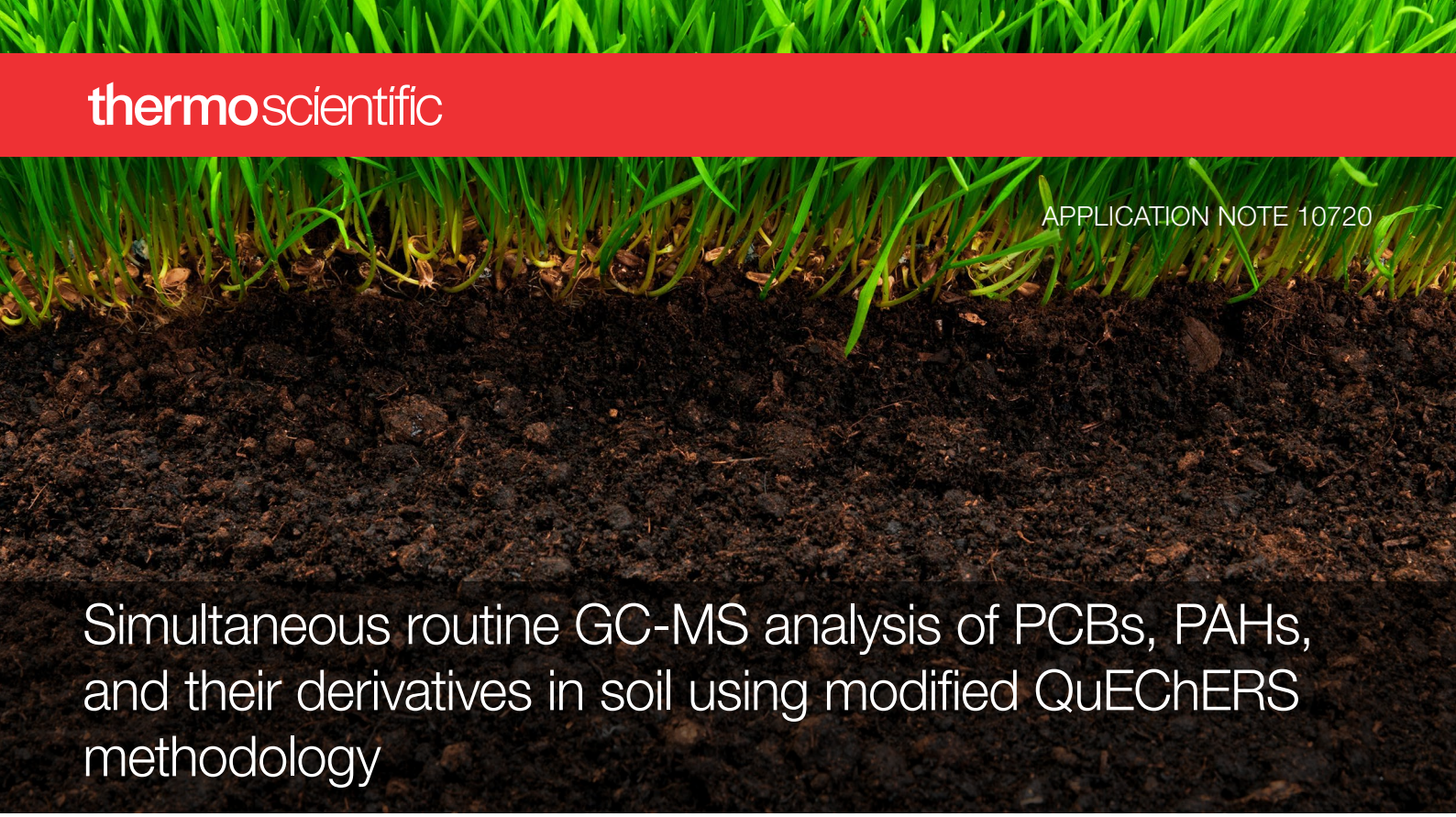

Simultaneous routine GC-MS analysis of PCBs, PAHs, and their derivatives in soil using modified QuEChERS methodology

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Keywords

Environmental analysis, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), QuEChERS, NeverVent technology, high sample throughput, robust, gas chromatography, single quadrupole mass spectrometry, sensitivity, routine, ISQ 7000, Chromeleon CDS

Goal

The purpose of this study was to assess the quantitative performance of the Thermo Scientific™ ISQ™ 7000 single quadrupole GC-MS system equipped with the ExtractaBrite electron ionization source and NeverVent™ Technology for the routine analysis of PAHs and PCBs using a quick, easy, cheap, effective, rugged, and safe (QuEChERS) method modified specifically for soil testing.

Introduction

Polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) are toxic organic compounds that can contaminate soils, air, sediments, and water as a result of natural and anthropogenic processes. PCBs and PAHs are resistant to environmental degradation and can be transported over long distances. Moreover, due to their lipophilicity these chemicals can undergo biomagnification and accumulation in the food chain and can pose significant health risks to humans. Their toxicity even at very low concentrations means that their presence in the environment needs to be monitored so that the risk of uptake of these compounds into the food chain and subsequently into human populations is minimized.

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More recently it has become apparent that oxidized and substituted derivatives of PAHs (such as oxy and methyl PAHs) have similar or increased toxicities compared to non-substituted versions; therefore, governments have already begun monitoring them in soil and particulate matter.[1,2] Nitrogen, sulfur, and oxygen containing polyaromatic heterocycles (NSO-PAHs) are another class of compounds that have gained interest due to their ubiquitous presence in the environment and lack of data on their toxicities.[2,3]

PCBs and PAHs (and derivatives) are usually analyzed by gas chromatography (GC) coupled to mass spectrometry (MS). The challenges for the analysis of PAHs and PCBs are the requirement for tedious, time-consuming, complicated, and costly sample preparation such as Sohxlet extraction. Often, long chromatographic separations (>40 min per sample) are required, which overall will result in low sample throughput and high cost of analysis.

In order to characterize an environmental sample, multiple methods are often employed for both the sample preparation and GC-MS analysis of these compounds. Having multiple chromatographic methods for the same sample increases both the requirement for labor and instrumentation and ultimately increases the cost per sample. In this application note we consolidated approaches for the rapid and cost-effective analysis of sixteen EPA PAHs, seven marker PCBs, three oxyPAHs, ten methylPAHs, and nine NSO-PAHs in soil samples. For this, a modified QuEChERS sample extraction and clean up was investigated. Chromatographic separation of target compounds was optimized for a <20 min/sample method using Restek's Pro ***EZ***GC™ chromatogram modeler, and detection was achieved using the ISQ 7000 GC-MS operated in electron ionization (EI) mode.

The evaluation of system robustness and method suitability for routine PAH and PCB GC-MS analysis, which was outside the scope of this application note, was assessed in separate experiments.[4]

Experimental

Preparation of solvent calibration curve, instrument detection limit (IDL) and limit of quantification (LOQ) standards

Calibration standards containing 45 native PCB, PAHs, methyl PAHs, oxyPAHs, PANHs, PASHs, and PAOHs at twelve concentration levels (Table 6. Appendix), and 14 (^{13}C-labeled) internal standards (Table 7. Appendix), were acquired from Fisher Scientific, AccuStandards, and Wellington Laboratories Inc. (Ontario, Canada).

For the calculation of IDLs and LOQs, the lowest concentration standard was serially diluted with n-hexane to 0.4, 0.6, 0.8, 1.0, 2.5, and 5.0 pg/µL.

Preparation of soil samples

Soil was freeze dried, homogenized, and sieved prior to a modified QuEChERS extraction and clean up procedure. The total QuEChERS sample preparation time was 2 hours. A summary of the QuEChERS methodology can be seen in Figure 1.

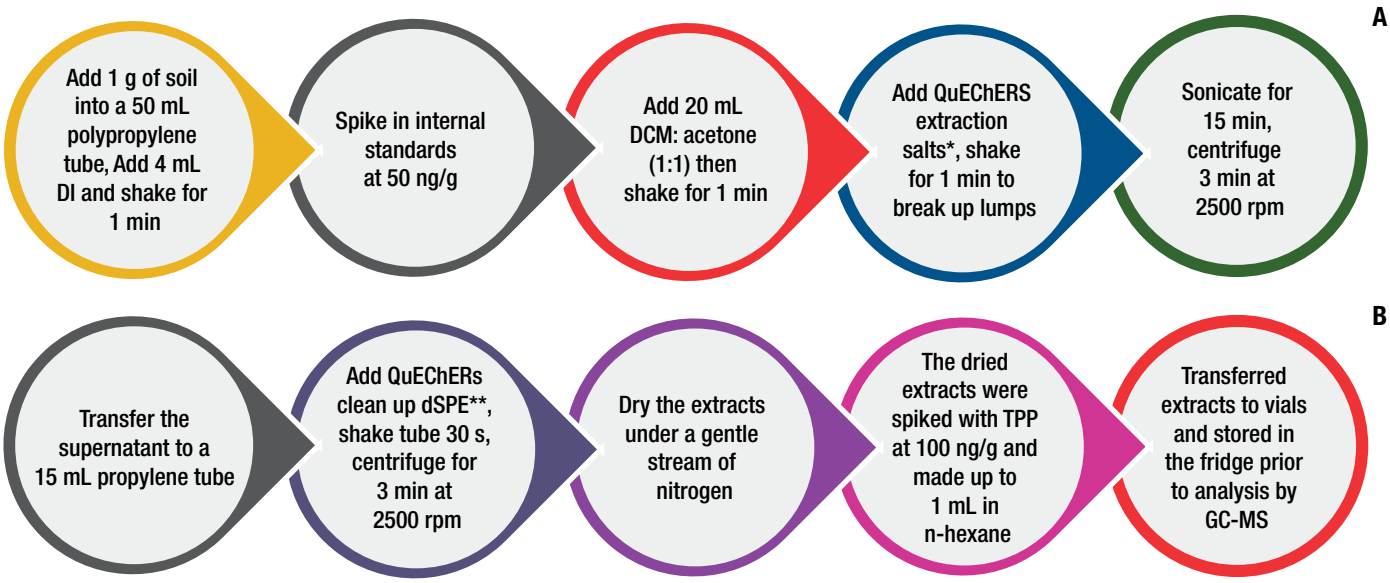


Figure 1. (A) QuEChERS extraction method used for soil analysis. *Thermo Fisher Scientific, P/N 60405-333, (4 g $MgSO_4$, 1 g NaCl, 0.5 g disodium citrate sesquihydrate, 1 g of trisodium citrate dihydrate); (B) QuEChERS dSPE method used for soil analysis. **Thermo Fisher Scientific, P/N 60105-215, (900 mg of $MgSO_4$ and 150 mg of PSA). DI = deionized water; TPP = triphenyl phosphate

GC-MS analysis

An ISQ 7000 single quadrupole GC-MS instrument equipped with the ExtractaBrite electron ionization source was coupled with a Thermo Scientific™ TRACE™ 1310 GC for this analysis. This configuration allows vent-free column changes and ionization source maintenance in under 2 minutes representing a 99% time saving versus traditional venting approaches, which can take up to 4 hours. This is achieved using state of the art NeverVent technology which increases laboratory productivity through the minimization of instrument downtime.

Liquid injections of the sample extracts were performed using a Thermo Scientific™ AI/AS 1310 Series Autosampler and chromatographic separation was achieved by a Thermo Scientific™ TraceGOLD™ TG-5 SilMS 30 m × 0.25 mm i.d. × 0.25 µm film (P/N 26096-1420) capillary column.[5] Additional details of instrument parameters are displayed in Tables 1 and 2. Full details of all consumables used can be found in Thermo Scientific™ AppsLab™ library (AN10720).

Data processing

Data were acquired using timed-SIM mode, processed, and reported using Thermo Scientific™ Chromeleon™ 7.2 Chromatography Data System (CDS) software, which allows instrument control, method development, and quantitative and qualitative analysis with customizable reporting all within one platform. eWorkflows™ are important tools for the routine testing laboratory that provide the ability to launch immediate sample analysis with pre-designed sequences ready for data acquisition, automatic data processing, and reporting. Labs requiring scalable and future-proof software solutions should consider Chromeleon CDS Enterprise software.

Table 1. GC and injector conditions. Full list of consumables and instrument can be found in AppsLab library.

TRACE 1310 GC parameters	
Injection volume (µL)	1.0
Liner	Single gooseneck with glass wool 4.0 mm × 6.3 mm × 78.5 mm (Thermo Scientific™ LinerGOLD™) (P/N 453A1925-UI)
Inlet (°C)	300
Inlet module and mode	SSL, Splitless
Splitless time (min)	1.0
Split flow (mL/min)	50.0
Septum purge flow (mL/min)	5.0
Carrier gas, flow rate (mL/min)	He, 1.2
Oven temperature program	
Temperature 1 (°C)	40
Hold time (min)	1.0
Temperature 2 (°C)	285
Rate (°C/min)	28
Hold time (min)	0
Temperature 3 (°C)	305
Rate (°C/min)	3
Hold time (min)	0
Temperature 4 (°C)	350
Rate (°C/min)	30
Hold time (min)	5
Total GC run time (min)	20

Table 2. Mass spectrometer conditions

ISQ 7000 EI GC-MS parameters	
Transfer line (°C)	350
Ion source (Ionization type)	ExtractaBrite (EI)
Ion source (°C)	350
Electron energy (eV)	70
Emission current (µA)	50
Acquisition mode	timed-SIM
Tuning parameters	EI SmartTune*

*SmartTune is an intelligent automatic tuning protocol that simplifies the MS tuning process. The user can set system sensitivity tolerances so that peak areas can be maintained throughout multiple weeks of analysis.

Results and discussion

Chromatography, selectivity, sensitivity, and linearity were evaluated using solvent-based standards. Assessment of recovery, selectivity, and sensitivity were performed in soil using a modified QuEChERS extraction method as described in the Experimental section.

Chromatography

All compounds were separated in under 20 minutes including excellent separation of the critical pairs in the 16 EPA PAH standard (i) phenanthrene/anthracene (ii) benzo[*a*]anthracene/chrysene (iii) benzo[*b*]fluoranthene/benzo[*k*]fluoranthene (Figure 2). As expected with fast multiresidue methods of this nature, some compound coelutions did occur in which case the data was reported as a sum of the combined area, this included (i) 1-ethylnapthanalene/2-ethylnapthalene (ii) 1,3-dimethylnapthalene/1,6-dimethylnapthalene. Due to the superior inertness of the TraceGOLD silphenylene GC columns, excellent peak shape was observed for all compounds including the strongly basic compound quinoline, which had a European Pharmacopeia (EP) asymmetry value of 1.0.[3]

Selectivity

Due to the diversity of sample matrices with various degrees of complexity, selectivity can be challenging in routine GC-MS analysis of soils. An example of sample complexity is shown in Figure 3 as an overlay of the TIC EI full scan of a sonicated unspiked QuEChERS soil extract (top chromatogram) and of timed SIM (bottom chromatogram) showing the incurred residues.

Carryover assessment

Carryover is a known issue when analyzing PCBs and PAHs (and derivatives) in soils. However, this problem was addressed by using a mixed needle wash solvent of dichloromethane: toluene: n-nonane (50:25:25). The SIM quantification and qualification ions for PCB-180 of the highest concentration injected standard at 500 pg on column (OC) (A) and the consecutive n-hexane blank (B) are shown below (Figure 4) with no detectable carryover observed in the blank.

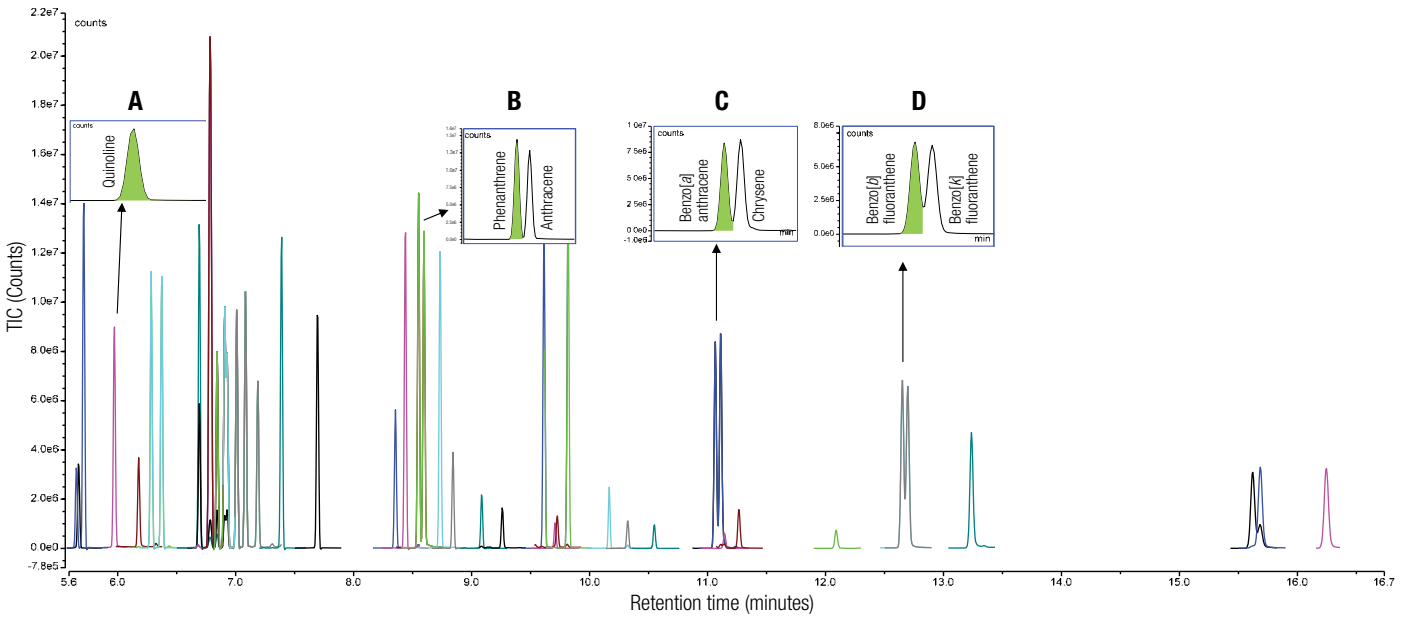


Figure 2. Chromatogram showing overlaid native PAHs and PCBs t-SIM XICs for a 50 pg/µL (50 pg on column (OC) solvent standard in n-hexane with excellent chromatographic peak shapes for all compounds in under 20 minutes run time. C^{13}-labeled internal standards were not displayed to show native peak shapes clearly. (A) Peak shape for nitrogen containing polyaromatic heterocycle quinoline with EP peak asymmetry of 1.0; (B) Resolution of critical components phenanthrene and anthracene with EP resolution of 1.5; (C) Resolution of critical components benzo(*a*) anthracene and chrysene with EP resolution of 1.3; (D) Resolution of critical components benzo[*b*]fluoranthene and benzo[*k*]fluoranthene with EP resolution of 1.0.

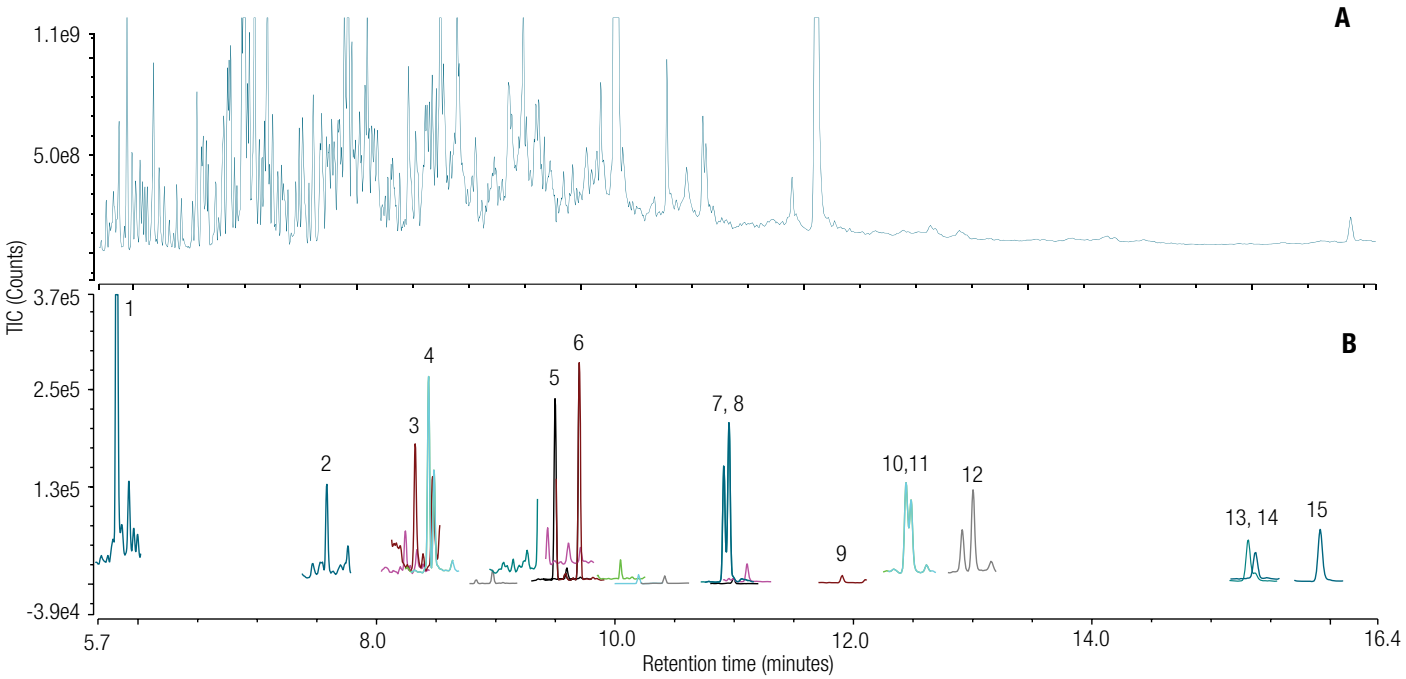


Figure 3. (A) QuEChERS soil extract unspiked, FS, *m/z*=50–550; (B) QuEChERS soil extract unspiked, t-SIM native incurred residue XICs; Incurred residues; 1=Quinoline, 2=Fluorene, 3=Dibenzothiophene, 4=Anthracene, 5=Fluoranthene, 6=Pyrene, 7=Benzo[*a*]anthracene, 8=Chrysene, 9=5,12-Napthacenequinone, 10=Benzo[*b*]fluoranthene, 11=Benzo[*k*]fluoranthene, 12=Benzo[*a*]pyrene, 13=Indeno[1,2,3-*cd*]pyrene, 14=Dibenzo[*a,h*]anthracene, 15=Benzo[*ghi*]perylene. C13-labeled internal standards were not displayed to show native peak shapes clearly.

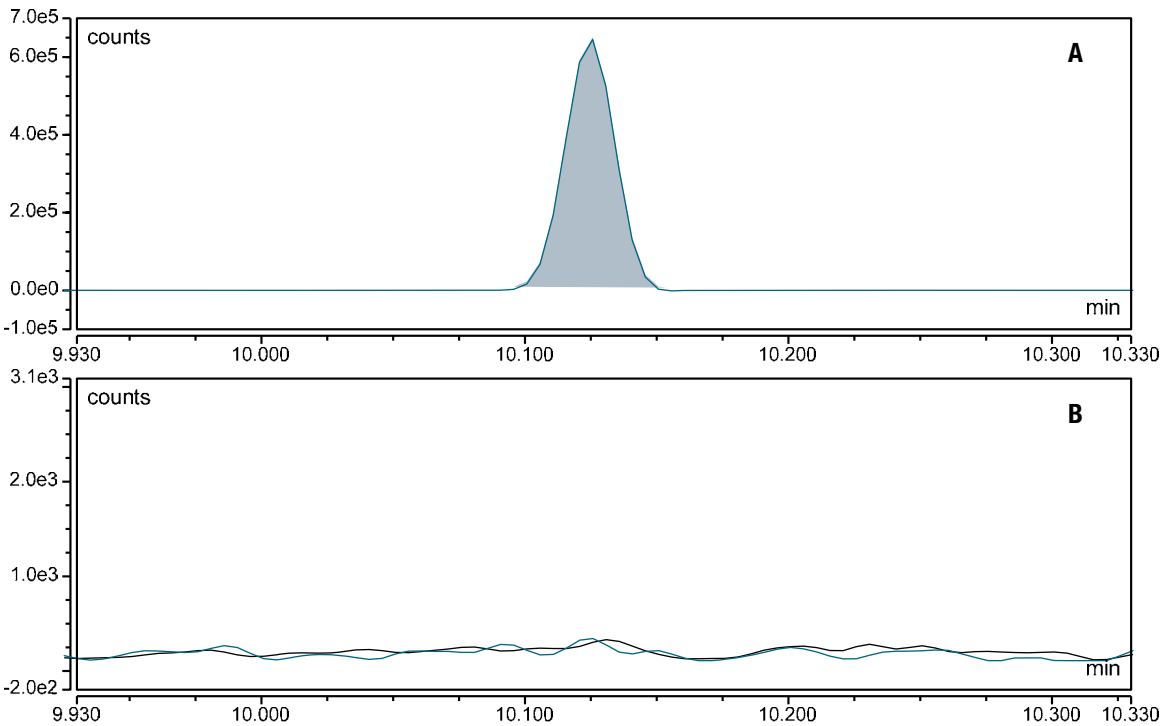


Figure 4. Chromatogram showing (A) overlaid SIM quantification and qualifier ions for the highest calibration standard for PCB-180, 500 pg OC, (B) overlaid SIM quantification and qualifier ions for PCB-180 in the consecutive n-hexane blank showing no detectable carryover. Data acquired in EI mode.

Sensitivity: determination of IDLs

To practically assess the IDLs, n=13 replicate injections of the lowest serially diluted solvent standard with a peak area RSD of <15% were used. The IDL was then calculated by considering the injected amount, peak area % RSD, and t-score of 2.681, corresponding to 12 (n-1) degrees of freedom at the 99% confidence interval (Figures 5 and 6). The method sensitivity is demonstrated for the highest molecular weight PAH compound analyzed, benzo(*ghi*)perylene (Figure 5). Here a 400 fg/µL (400 fg OC) solvent standard shows excellent signal precision with peak area repeatability <15% RSD at low ppb levels (IDL equivalent to 0.13 µg/kg) in sample extracts). Excellent peak shape is also observed for this high boiling compound (BP = 550 °C), which is due to the inertness of the TraceGOLD TG-5 SilMS column coupled with the highly uniform heating profile of the newly designed ISQ 7000 transfer line. These factors result in less peak tailing for low volatility, high boiling compounds such as heavier PAHs and PCBs and make accurate integration possible. The IDL values calculated ranged from 56 to 2004 fg OC (corresponding to 0.06–2.00 µg/kg in sample).

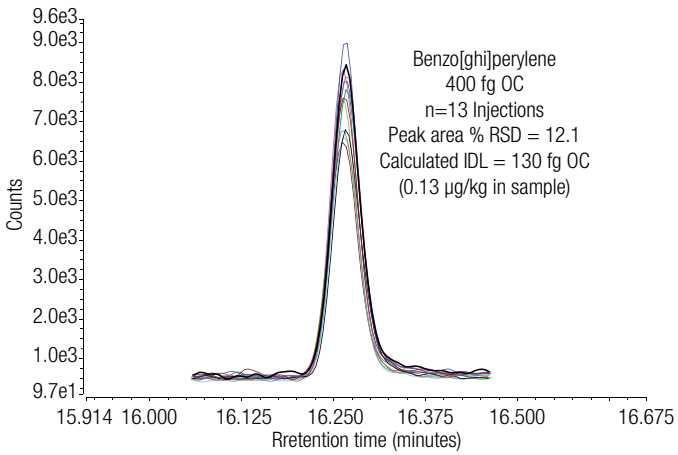


Figure 5. Overlaid quantification XICs (276 *m/z*) from n=13 consecutive injections of a 400 fg/µL benzo[*ghi*]perylene solvent standard (calculated IDL corresponding to 0.13 µg/kg in sample). No data smoothing was used, and data were acquired in timed-SIM mode.

Sensitivity: determination of limit of quantitation (LOQ)

Method LOQs were calculated using serially diluted calibration standards described in the IDL section. Thirteen (n=13) replicate injections of each of the diluted standards ranging between 0.4 pg/µL and 5.0 pg/µL were performed (equivalent to 0.4–5.0 µg/kg in sample) (Table 3).

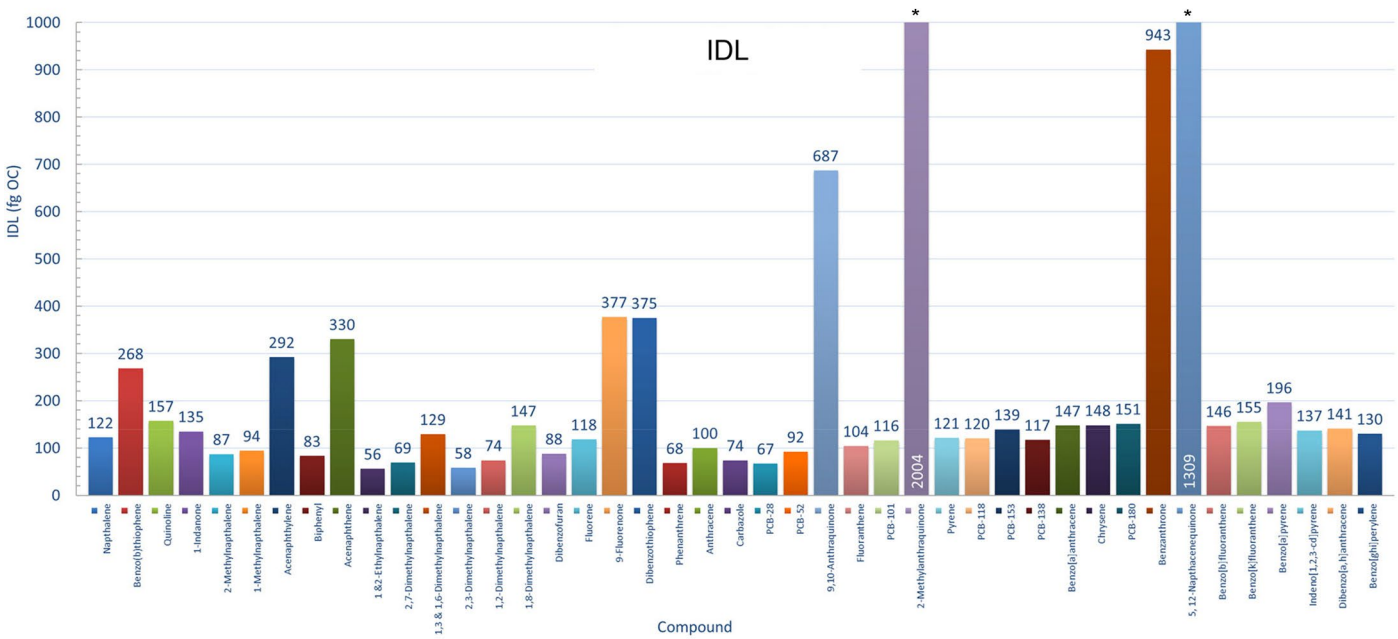


Figure 6. Graph showing individual IDLs in fg OC for 45 native PCB, PAH, methyl PAH, oxyPAH, and NSO-PAHs calculated from n=13 replicate injections of the lowest serially diluted standards. *oxyPAHs are known to degrade in the liner, meaning that the calculated IDLs are higher than that typically seen for other types of PAHs.

Table 3. Method LOQs were estimated from the lowest serially diluted calibration standard, prepared as detailed in the experimental section, which pass the criteria. Thirteen replicate injections of each of the diluted standards ranging between 0.4 pg/µL and 5.0 pg/µL were performed. The criteria used to assess individual LOQs were (i) measured ion ratio ±30% compared to the target ion ratio calculated form the average ion ratio across the calibration range (ii) peak area <15% RSD.

Native name	Amount injected (pg OC)	Target ion ratio %	Mean measured ion ratio %	Mean % Deviation	Peak area % RSD	LOQ (pg OC)	LOQ (µg/kg)
Naphthalene	1.0	11.0	11.0	0%	4	1.0	1.0
Benzo(b)thiophene	2.5	14.8	16.6	12%	2	2.5	2.5
Quinoline	0.4	34.8	35.4	2%	14	0.4	0.4
1-Indanone	1.0	98.3	87.6	-11%	13	1.0	1.0
2-Methylnaphthalene	0.4	108.4	100.7	-7%	9	0.4	0.4
1-Methylnaphthalene	0.4	106.1	90.0	-15%	8	0.4	0.4
Acenaphthylene	2.5	69.7	73.4	5%	5	2.5	2.5
Biphenyl	0.4	43.7	39.1	-11%	6	0.4	0.4
Acenaphthene	2.5	108.8	103.1	-5%	7	2.5	2.5
1-Ethylnaphthalene+2-Ethylnaphthalene	0.4	38.4	34.9	-9%	7	0.4	0.4
2,7-Dimethylnaphthalene	0.4	120.6	123.5	2%	6	0.4	0.4
1,3-Dimethylnaphthalene+1,6-Dimethylnaphthalene	0.4	99.5	106.6	7%	12	0.4	0.4
2,3-Dimethylnaphthalene	0.4	87.8	94.4	8%	5	0.4	0.4
1,2-Dimethylnaphthalene	0.4	69.1	55.1	-20%	7	0.4	0.4
1,8-Dimethylnaphthalene	2.5	100.2	88.5	-12%	3	2.5	2.5
Dibenzofuran	0.4	44.3	47.9	8%	8	0.4	0.4
Fluorene	0.4	100.1	114.9	15%	7	0.4	0.4
9-Fluorenone	1.0	52.7	55.3	5%	14	1.0	1.0
Dibenzothiophene	5.0	20.3	20.2	-1%	5	5.0	5.0
Phenanthrene	0.4	20.6	23.8	16%	6	0.4	0.4
Anthracene	0.4	20.1	21.3	6%	9	0.4	0.4
Carbazole	1.0	15.8	15.9	1%	6	1.0	1.0
PCB-28	0.4	95.8	93.2	-3%	6	0.4	0.4
PCB-52	0.4	78.9	78.5	-1%	9	0.4	0.4
9,10-Anthraquinone	5.0	109.8	113.8	4%	6	5.0	5.0
Fluoranthene	0.4	22.2	23.0	4%	10	0.4	0.4
PCB-101	0.4	62.7	66.9	7%	11	0.4	0.4
2-Methylanthraquinone	5.0	49.4	53.1	7%	13	5.0	5.0
Pyrene	0.4	26.9	29.8	11%	11	0.4	0.4
PCB-118	0.4	61.8	62.5	1%	11	0.4	0.4
PCB-153	0.4	79.3	74.7	-6%	13	0.4	0.4
PCB-138	0.4	79.9	73.6	-8%	11	0.4	0.4
Benzo[*a*]anthracene	0.4	20.8	23.6	14%	14	0.4	0.4
Chrysene	0.4	23.6	23.0	-2%	14	0.4	0.4
PCB-180	0.4	95.3	101.6	7%	14	0.4	0.4
Benzanthrone	5.0	62.8	71.1	13%	3	5.0	5.0
5, 12-Naphthacenequinone	5.0	74.3	79.6	7%	6	5.0	5.0
Benzo[*b*]fluoranthene	0.4	27.2	29.7	9%	14	0.4	0.4
Benzo[*k*]fluoranthene	0.4	25.4	29.4	16%	14	0.4	0.4
Benzo[*a*]pyrene	0.4	27.0	28.5	6%	14	0.4	0.4
Indeno[1,2,3-*cd*]pyrene	0.4	39.6	34.1	-14%	13	0.4	0.4
Dibenzo[*a,h*]anthracene	0.4	25.7	26.6	3%	13	0.4	0.4
Benzo[*ghi*]perylene	0.4	43.2	35.4	-18%	14	0.4	0.4

The criteria used to assess individual LOQs were:

- Ion ratios within ±30% of the expected values calculated as an average across a calibration curve ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in sample, Figure 7)
- Peak area repeatability of <15% RSD

Linearity

Linearity was determined using solvent standards at concentrations 0.1–500 pg/µL. The calibration of each compound was performed using the average calibration factor function (AvCF) in Chromeleon CDS software over three injections at each concentration level (Figure 8).

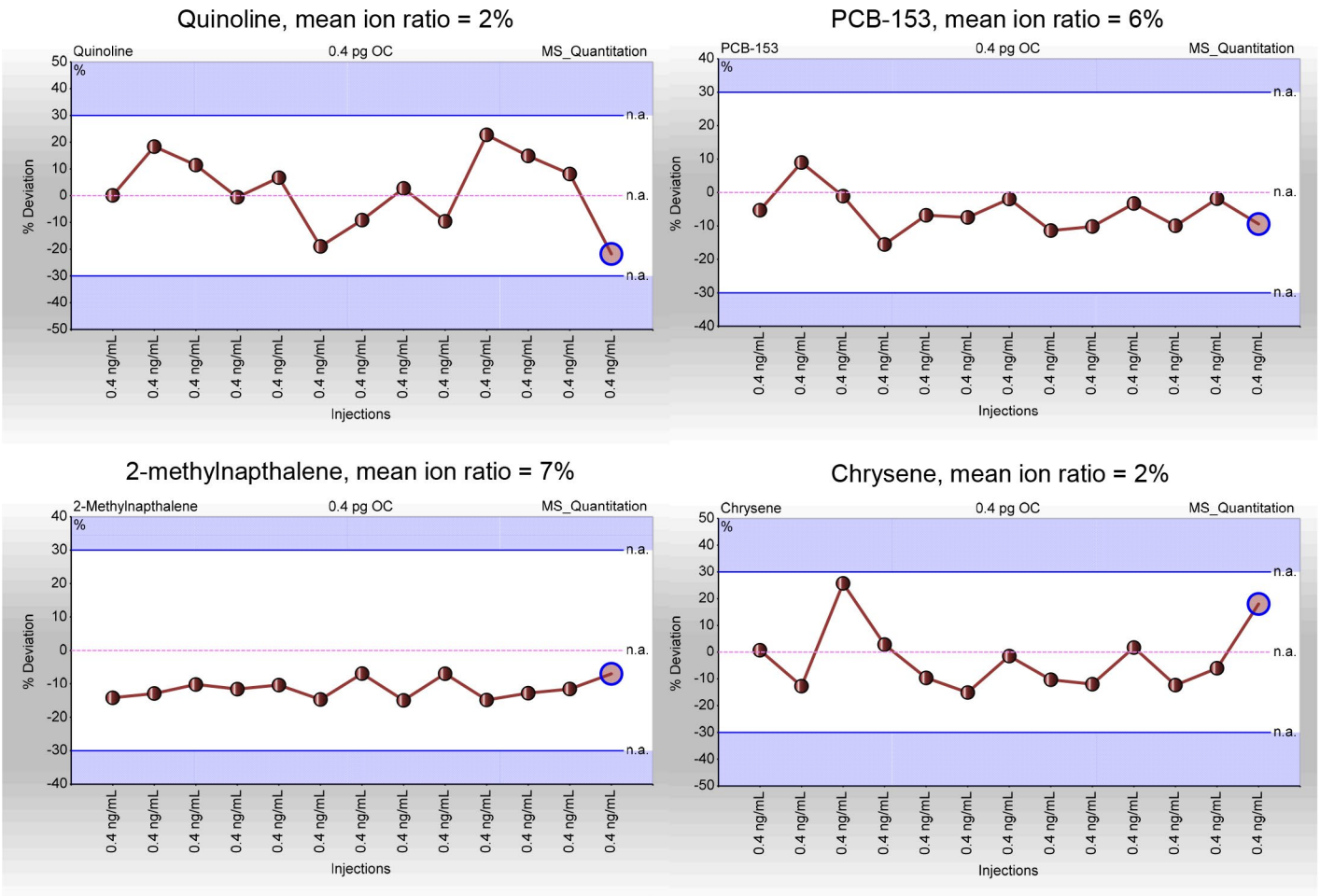


Figure 7. Ion ratio consistency demonstrated for selected PAHs and PCBs over n=13 replicate injections of a solvent standard at the LOQ level (in this examples LOQ level was 0.4 pg OC). The average ion ratio % deviation calculated from the calibration range is displayed as a pink dotted line in the center. The ±30% upper and lower ion ratio tolerance windows are also defined, and for all PAHs and PCBs the ion ratio % deviation for injections were within specification illustrated using Chromeleon CDS software interactive charts.

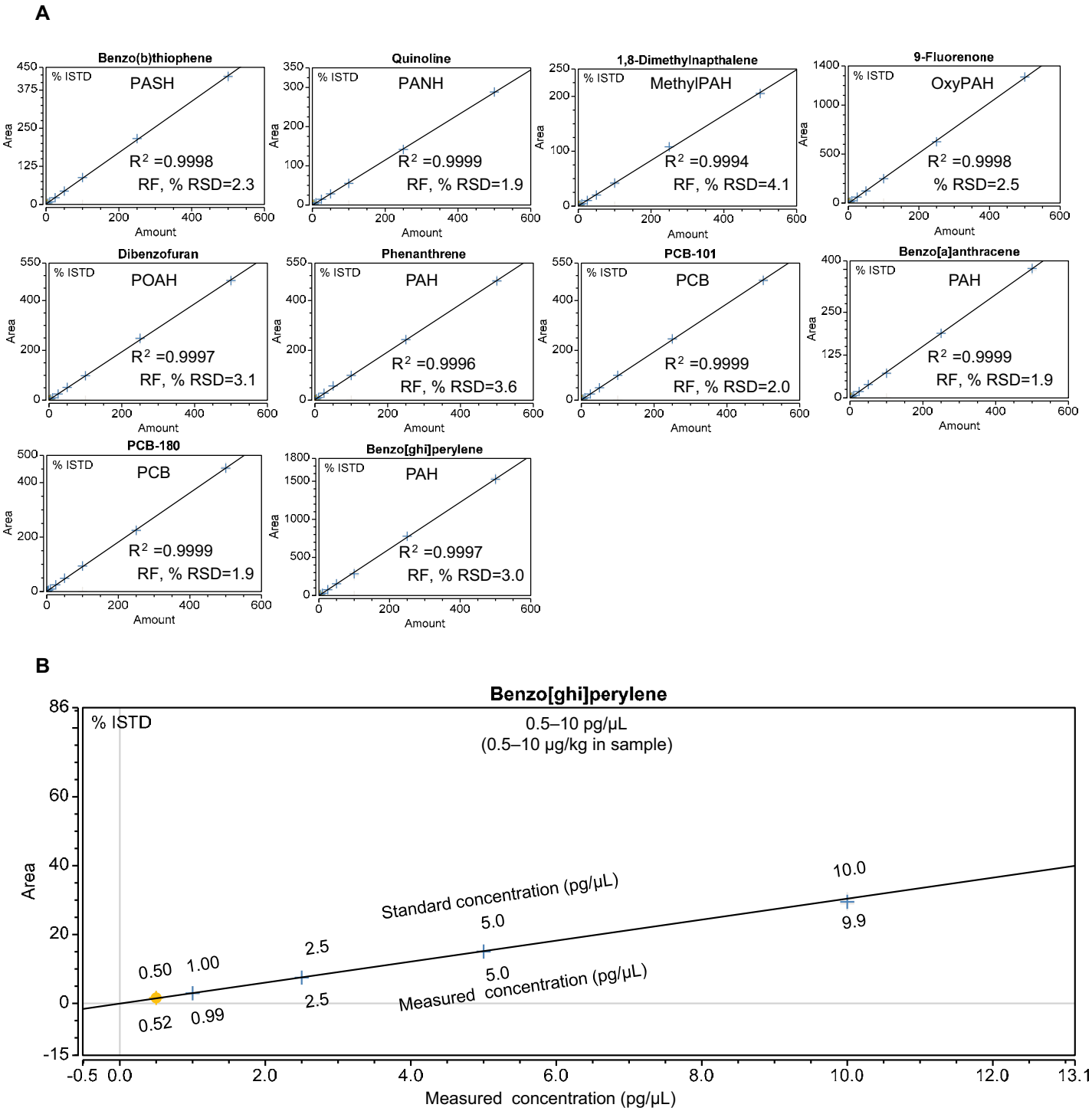


Figure 8. (A) Linearity of example PAHs and PCBs as demonstrated using solvent-based calibration curves ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in sample). Average calibration factor function (AvCF) was used in Chromeleon CDS software and three replicate injections at each concentration with internal standard adjustment were performed. Coefficient of determination (R^2) and response factor % RSD values (RF, % RSD) are displayed. (B) A magnified region of the calibration for benzo[*ghi*]perylene ranging from 0.5 to 10 pg/µL is shown (corresponding to 0.1–500 µg/kg in sample), demonstrating excellent precision and accuracy for triplicate injections per point.

All compounds show excellent linear responses with coefficients of determination $R^2 \geq 0.998$, and response factor % RSD values (RF, % RSD) across the calibration range <10%. The R^2 values ranged from 0.9989 to 0.9999 with an average value of 0.999. (Table 4).

Table 4. Coefficient of determination (R^2) and residual average response factor (% RSD)

Compound	Compound type	R^2	AvCF % RSD
Naphthalene	PAH	0.9994	4.1
Acenaphthene	PAH	0.9995	3.4
Acenaphthylene	PAH	0.9997	2.9
Biphenyl	PAH	0.9997	3.2
Fluorene	PAH	0.9995	3.8
Phenanthrene	PAH	0.9996	3.6
Anthracene	PAH	0.9997	3.4
Fluoranthene	PAH	0.9997	2.8
Pyrene	PAH	0.9994	4.6
Benzo[*a*]anthracene	PAH	0.9999	1.9
Chrysene	PAH	0.9998	2.5
Benzo[*b*]fluoranthene	PAH	0.9991	5.5
Benzo[*k*]fluoranthene	PAH	0.9990	5.6
Benzo[*a*]pyrene	PAH	0.9980	8.0
Indeno[1,2,3-*cd*]pyrene	PAH	0.9997	3.3
Dibenzo[*a,h*]anthracene	PAH	0.9996	3.3
Benzo[*ghi*]perylene	PAH	0.9997	3.0
2-Methylnaphthalene	methylPAH	0.9998	2.7
1-Methylnaphthalene	methylPAH	0.9999	1.4
2,7-Dimethylnaphthalene	methylPAH	0.9996	3.7
1,3-Dimethylnaphthalene+ 1,6-Dimethylnaphthalene	methylPAH	0.9996	3.6
2,3-Dimethylnaphthalene	methylPAH	0.9996	3.8
1,2-Dimethylnaphthalene	methylPAH	0.9992	4.7
1,8-Dimethylnaphthalene	methylPAH	0.9994	4.2
PCB-28	PCB	0.9989	6.5
PCB-52	PCB	0.9989	6.2
PCB-101	PCB	0.9999	2.0
PCB-118	PCB	0.9999	1.4
PCB-153	PCB	0.9999	2.2
PCB-138	PCB	0.9999	2.1
PCB-180	PCB	0.9999	1.9
Benzo[*b*]thiophene	PASH	0.9998	2.3
Dibenzothiophene	PASH	0.9991	5.5
1-Ethylnaphthalene+2-Ethylnaphthalene	ethylPAH	0.9997	2.9
Quinoline	PANH	0.9999	1.8
1-Indanone	PAOH	0.9999	1.8
Dibenzofuran	PAOH	0.9997	3.1
Carbazole	PAOH	0.9992	5.4
9,10-Anthraquinone	PAOH	0.9999	1.6
2-Methylanthraquinone	PAOH	0.9999	1.7
9-Fluorenone	oxyPAH	0.9998	2.5
Benzanthrone	oxyPAH	0.9994	4.8
5,12-Naphthacenequinone	oxyPAH	0.9998	2.7
	Mean (all compounds)	0.9996	3.4
	Min (all compounds)	0.9980	1.4
	Max (all compounds)	0.9999	8.0

Recoveries

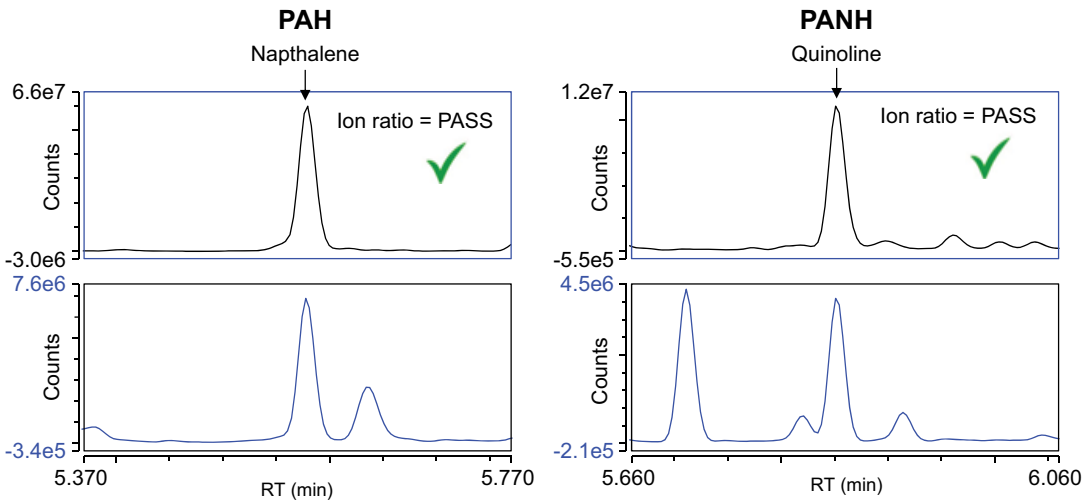
Seven technical replicate QuEChERS extractions, performed on soil spiked with deuterated internal standards at 50 ng/g added prior to extraction, were used to assess % recovery (see Figure 1 for sample preparation details). Triphenyl phosphate was added as a syringe standard post extraction spiked at 100 ng/g to adjust for potential injection variability (Table 5). All compounds show good recovery with average internal standard recovery of 75% (Table 5). Lower boiling point compounds, such as naphthalene-d_8, had lower recoveries that could be explained by losses during the solvent evaporation phase. Although the recovery of such compounds is low, precision of measurement over n=7 technical replicate extractions was <15% RSD for all compounds and the majority being <5%. This clearly demonstrates that the QuEChERS extraction and dSPE procedure method is highly reproducible and therefore suitable for routine testing laboratories. The total QuEChERS sample preparation time was 2 hours, which compared to typical Soxhlet extractions of 24–48 hours is a significant time (and cost) savings of 10–20×.

Quantification of PAHs and PCBs in QuEChERS soil extracts

Soil samples, extracted using a revised QuEChERS method as described in Figure 1, were analyzed for native incurred residues. The quantitative performance of the method in terms of sensitivity and selectivity is highlighted below with examples of low level native incurred residues (Figures 9 and 10).

Table 5. QuEChERS soil extraction IS % recovery data

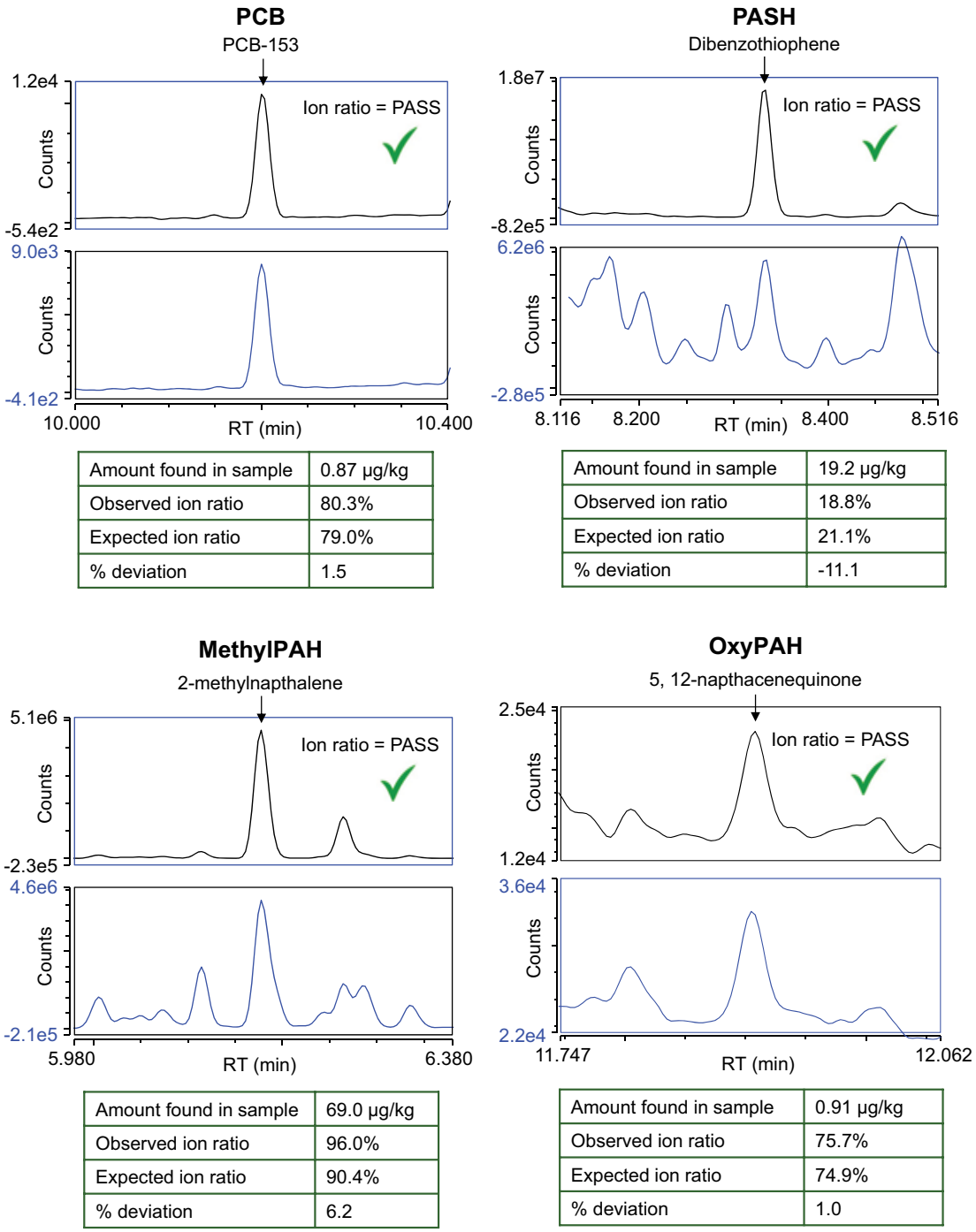
Compound	IS spiked recovery %									
	1	2	3	4	5	6	7	Mean	STDEV	% RSD
Naphthalene-d_8	47.6	48.6	52.5	49.7	58.2	54.5	47.5	51	4.026	7.9%
Quinoline-d_7	63.3	51.3	66.3	54.6	66.3	63.7	58.7	61	5.888	9.7%
Dibenzofuran-d_8	80.4	58.8	67.8	63.4	68.0	67.8	57.9	66	7.543	11.4%
9-Fluorenone-d_8	92.6	91.9	101.4	99.7	100.4	100.3	92.4	97	4.390	4.5%
Dibenzothiophene-d_8	62.9	62.3	66.8	66.2	66.7	68.1	60.5	65	2.852	4.4%
PCB-28L	58.3	58.0	61.4	61.2	60.2	61.3	54.4	59	2.566	4.3%
o-Terphenyl	76.5	70.4	75.8	75.5	76.1	77.8	70.3	75	3.013	4.0%
PCB-52L	63.8	61.4	65.9	64.0	65.0	65.2	60.3	64	2.070	3.3%
9,10-Anthraquinone-d_8	112.4	111.0	117.7	118.1	118.1	118.4	112.0	115	3.386	2.9%
PCB-101L	78.8	72.5	81.6	78.7	78.7	80.8	76.8	78	2.989	3.8%
Pyrene-d_{10}	110.9	114.7	103.9	109.2	83.9	82.2	85.6	99	14.172	14.4%
PCB-118L	72.4	69.4	74.9	71.9	74.2	76.3	70.0	73	2.548	3.5%
PCB-153L	74.7	72.1	75.7	75.9	76.5	76.3	72.0	75	1.927	2.6%
PCB-138L	70.4	65.8	68.3	67.6	67.8	69.0	66.0	68	1.618	2.4%
PCB-180L	72.0	68.6	71.9	70.1	72.4	72.2	68.4	71	1.745	2.5%
Perylene-d_{12}	75.6	72.5	74.3	72.8	75.0	75.5	72.8	74	1.354	1.8%



Amount found in sample	593 µg/kg
Observed ion ratio	12.4%
Expected ion ratio	11.9%
% deviation	4.9

Amount found in sample	108 µg/kg
Observed ion ratio	35.2%
Expected ion ratio	36.6%
% deviation	-3.8

Figure 9. Examples of SIM XIC chromatograms (quantification ion in black and confirmation ion in blue) for naphthalene in soil (left) and quinoline in soil (right). Below each of the SIM chromatograms the following is annotated: (i) amount found in sample as µg/kg, (ii) measured ion ratio, (iii) expected ion ratio determined from the average of the calibration, and (iv) % deviation of measured ion ratio versus the expected ion ratio.



Amount found in sample	0.87 µg/kg
Observed ion ratio	80.3%
Expected ion ratio	79.0%
% deviation	1.5

Amount found in sample	19.2 µg/kg
Observed ion ratio	18.8%
Expected ion ratio	21.1%
% deviation	-11.1

Amount found in sample	69.0 µg/kg
Observed ion ratio	96.0%
Expected ion ratio	90.4%
% deviation	6.2

Amount found in sample	0.91 µg/kg
Observed ion ratio	75.7%
Expected ion ratio	74.9%
% deviation	1.0

Figure 10. Examples of SIM XIC chromatograms (quantification in black and confirmation ions in blue) for PCB-153 in soil (top left), dibenzothiophene in soil (top right), 2-methylnaphthalene in soil (bottom left) and 5, 12-naphthacenequinone in soil (bottom right). Below each of the chromatograms the following is annotated: (i) amount found in sample in µg/kg, (ii) observed ion ratio between quantification and primary confirmation ion, (iii) expected ion ratio calculated from the average of the calibration, and (iv) % deviation of observed ion ratio versus the expected ion ratio.

In summary, the results obtained in these experiments demonstrate that a consolidated compound class method using a modified QuEChERS sample preparation can be used to quantify PAHs and PCBs in soils. In the case of PCB-153, low levels of incurred residues of 0.87 µg/kg were detected and quantified within an ion ratio deviation from the calibration of only 1.5% with minimal matrix interferences. Other compound classes, such as oxyPAHs were detected below their LOQ with excellent peak asymmetry and selectivity in matrix.

Conclusions

The results of the experiments described here demonstrate the following:

- Excellent chromatographic separation and overall analytical performance were attained for the analysis of PAHs and PCBs in soil in <20 min, allowing for an increase in sample throughput of 4× compared to existing chromatographic methods.[3]
- Exceptional system sensitivity was achieved using the ISQ 7000 GC-MS with the ExtractaBrite source, with the IDLs values calculated for 45 native compounds ranging from 60 to 2000 fg OC (corresponding to 0.06–2.00 µg/kg in sample).
- LOQs ranged from 0.4 to 5.0 µg/kg in soil as determined from n=13 repeat injections of the lowest serially diluted standard that satisfied the following acceptance criteria:
  - Ion ratios within ±30 % of the expected values calculated as an average across a calibration curve ranging from 0.1 to 500 pg/µL (equivalent to 0.4–5.0 µg/kg in sample)
  - Peak area repeatability of <15% RSD
- Linearity achieved across a calibration range of 0.1–500 pg/µL (corresponding to 0.1–500 µg/kg in soil) showed coefficient of determination values of $R^2 \geq 0.998$ and residuals <10%.
- All compounds show good recovery overall with the average internal standard recovery 75%, and precision of the seven technical replicate extractions <15% RSD for all compounds with the majority <5% RSD.
- Increased sample throughput of up to 20× can be realized by using a modified QuEChERS method compared to traditional Sohxlet extraction methods, saving cost and time.
- Low level quantitative performance in soil was excellent as demonstrated by the closeness of the ion ratios compared to expected values when used for confirmation of low-level incurred residues in soil such as PAHs, PCBs, and oxyPAHs.

Taken together these results demonstrate that modified QuEChERS methods and the AI/AS 1310 autosampler in combination with the ISQ 7000 GC-MS system's NeverVent technology offer significant time saving possibilities. This provides an ideal solution for routine laboratories looking to consolidate GC-MS methods for the analysis of environmental samples for PAHs and PCBs in a cost-effective manner with excellent quantitative performance.

References

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2. Sun, Z.; Zhu, Y.; Zhou, S.; Liu, W.; Zeng, E.Y.; Wang, X.; Xing, B.; Tao, S. Occurrence of nitro- and oxy-PAHs in agricultural soils in eastern China and excess lifetime cancer risks from human exposure through soil ingestion. *Environ Int.* **2017,** *108,* 261–270.
3. Anderson, J.T.; Achten, C. Time to say Goodbye to the 16 EPA PAHs? Toward an up-to-date use of PACs for environmental purposes. *Polycyclic Aromatic Compounds,* **2015,** *35,* 330–354.
4. Thermo Scientific Technical Note 10721: Routine and robust analysis of PAHs and PCBs in soil by single quadrupole GC-MS, **2019.**
5. Thermo Scientific Application Note 21735: Ultra-inert low bleed GC columns with advanced silphenylene polymer technology, 2017.

Appendix

Table 6. Details of 45 native compounds analyzed, including compound type, CAS number, and calibration range

Native standard	Compound type	CAS Number	Calibration range (ng/mL)
Napthalene	PAH	91-20-3	0.1–500
Benzo[*b*]thiophene	PASH	95-15-8	
Quinoline	PANH	91-22-5	
1-Indanone	PAOH	83-33-0	
2-Methylnapthalene	methylPAH	91-57-6	
1-Methylnapthalene	methylPAH	90-12-0	
Biphenyl	aromatic	92-52-4	
Acenaphthylene	PAH	208-96-8	
1-Ethylnapthalene	methylPAH	1127-76-0	
2-Ethylnapthalene	methylPAH	939-27-5	
Acenaphthene	PAH	83-32-9	
2,7-Dimethylnapthalene	methylPAH	582-16-1	
1,3-Dimethylnapthalene	methylPAH	575-41-7	
1,6-Dimethylnapthalene	methylPAH	575-43-9	
2,3-Dimethylnapthalene	methylPAH	581-40-8	
1,2-Dimethylnapthalene	methylPAH	573-98-8	
1,8-Dimethylnapthalene	methylPAH	569-41-5	
Dibenzofuran	PAOH	132-64-9	
Fluorene	PAH	86-73-7	
9-Fluorenone	oxyPAH	486-25-9	
Dibenzothiophene	PASH	132-65-0	
Phenanthrene	PAH	85-01-8	
Anthracene	PAH	120-12-7	
Carbazole	PAOH	86-74-8	
PCB-28	PCB	7012-37-5	
PCB-52	PCB	35693-99-3	
9,10-Anthraquinone	PAOH	84-65-1	
Fluoranthene	PAH	206-44-0	
PCB-101	PCB	37680-73-2	
2-Methylanthraquinone	PAOH	84-54-8	
Pyrene	PAH	129-00-0	
PCB-118	PCB	31508-00-6	
PCB-153	PCB	35065-27-1	
PCB-138	PCB	35065-28-2	
Benzo[*a*]anthracene	PAH	56-55-3	
Chrysene	PAH	218-01-9	
PCB-180	PCB	35065-29-3	
Benzanthrone	oxyPAH	82-05-3	
5,12-Napthacenequinone	oxyPAH	1090-13-7	
Benzo[*b*]fluoranthene	PAH	205-99-2	
Benzo[*k*]fluoranthene	PAH	207-08-9	
Benzo[*a*]pyrene	PAH	50-32-8	
Indeno[1,2,3-*cd*]pyrene	PAH	193-39-5	
Dibenzo[*a,h*]anthracene	PAH	53-70-3	
Benzo[*ghi*]perylene	PAH	191-24-2	

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Table 7. Details of the 14 internal standards, including compound type, CAS number, and concentration (suffix "L" indicates mass-labeled)

Internal standard	Compound type	CAS Number	Concentration (ng/mL)
Napthalene-d_8	PAH	1146-65-2	100
Dibenzofuran-d_8	PAOH	93952-04-6	
9-Fluorenone-d_8	oxyPAH	137219-34-2	
Pyrene-d_{10}	PAH	1718-52-1	
PCB-28L	PCB	7012-37-5	
PCB-52L	PCB	35693-99-3	
PCB-101L	PCB	37680-73-2	
PCB-118L	PCB	31508-00-6	
PCB-153L	PCB	35065-27-1	
PCB-138L	PCB	35065-28-2	
PCB-180L	PCB	35065-29-3	
Quinoline-d_7	PANH	34071-94-8	
o-Terphenyl	aromatic	84-15-1	
Perylene-d_{12}	PAH	1520-96-3	

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