Application of GC–Triple Quadrupole MS in the Quantitative Confirmation of Polycyclic Aromatic Hydrocarbons and Phthalic Acid Esters in Soil

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Abstract

A new multi-residue method has been developed and validated for the simultaneous analysis of 34 polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PAEs) in soil at trace levels by gas chromatography coupled to triple quadrupole mass spectrometry. Microwave extraction and solid-phase extraction have been employed prior to gas chromatography tandem mass spectrometry analysis. Quality parameters have been established using matrix spike and reference material IRM 104A. Average recoveries of the 34 organic compounds spiked at 5 µg/kg into soils are typically in the range of 66.59–122.07% with relative standard deviations generally less than 20%. Limits of detection (LODs) for PAEs are ≤ 0.84 µg/kg, and limits of quantification (LOQs) ranged from 0.13 to 2.81 µg/kg. LODs for PAHs are ≤ 0.51 µg/kg, and LOQs ranged from 0.02 to 1.81 µg/kg.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PAEs) are endocrine disrupting chemicals (1), which were highlighted as a problem in the early 90s. Several PAEs are harmful to human health, leading to the instability of internal secretions and procreation abilities (2,3). PAHs are classified as carcinogenic because the metabolites of PAHs present in the liver can bind to DNA and proteins and start mutagenic processes in the cells (4). Soil is the primary environmental reservoir for semivolatile organic compounds such as PAHs and PAEs in the terrestrial environment. To quantitatively evaluate the fate of these chemicals for a proper ecological risk assessment, environmental monitoring methods have to be adopted to analyze the concentration levels of these compounds in soil.

PAHs and PAEs are commonly analyzed by gas chromatography with flame-ionization detector (GC–FID), GC coupled with mass spectrometer (GC–MS), and by liquid chromatography (LC) coupled with fluorescence detector (FLD) and UV-diode array detector (UV–DAD) (5–8). The identification of target analytes by GC–FID relies solely on their retention time (t_R). Therefore, it lacks enough information to use in confirmation. For high-performance liquid chromatography (HPLC)–FLD and HPLC–UV–DAD, the use of absorption and selective fluorescence spectrums can improve the accuracy of qualification to some extent. But the complexity of the matrix may easily introduce much interference such as co-elution and prevent accurate quantification and qualification of those organic pollutants that are present in environmental soils at trace level. The application of MS provides higher specificity as it adds qualitative information for analytes identification. The confirmation from the MS spectra was carried out by applying the identification point criteria (IPs) established in the European Commission Decision 2002/657/EC. Briefly, this decision introduces the use of a number of IPs depending on the class of compound analyzed and the spectrometric technique used. As a rule, a minimum of three IPs are requested. While comparing triple quadrupole analyzer (QqQ) with single quadrupole analyzer, the product ion is more specific than the ion in the simple MS spectrum as the former is connected with the known precursor ion. One ion in simple MS spectrum only earns one IP while one precursor ion and two product ions in MS–MS earn four IP. It means QqQ may provide more accurate quantification and confirmation in trace analysis with complex matrix. While comparing triple quadrupole analyzer (QqQ) with ion trap analyzer, the higher scan speed (9) of QqQ in multiple reaction monitoring (MRM) mode means more sensitivity and relatively less running time to develop a multi-residue method.

In this paper, microwave-assisted extraction (MAE) and solid-phase extraction (SPE) were used for extraction and clean-up. And a simple, rapid and sensitive analytical methodology had been developed to simultaneous determine 34 PAHs and PAEs in soils with GC–QqQ-MS–MS.

Materials and Methods

Reagents and standards

Solvents used in this study are of ABSOLV-grade: methylene chloride (DCM), *n*-hexane (HEX) (Fluka, Buchs, Switzerland), and acetone (ACE) (Fisher, Hampton, NJ). The standard mixture

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Table I. Retention Time (t_R) and MS–MS Conditions

Seg	Compund	t_R (min)	Precursor ion (*m/z*)	Product ion (*m/z*) (collision energy, eV)	Precursor ion (*m/z*)	Product ion (*m/z*) (collision energy, eV)
1	Naphthalene-d_8 (IS)	4.907	136	84(20)	136	108(20)
	Naphthalene	4.931	128 [M]	77(25) [-C_4H_3]	128 [M]	102(15)[-C_2H_2]
2	Phthalic acid, bis-mehyl ester	6.351	194 [M]	163(10) [-CH_3O]	163 [$C_9H_7O_3$]$^+$	133(10)[-CH_2O]
	Acenaphthylene	6.453	152 [M]	126(25) [-C_2H_2]	152 [M]	76(35)[-C_6H_4]
	Acenaphthene	6.745	152 [M]	126(25) [-C_2H_2]	152 [M]	76(35) [-C_6H_4]
3	Phthalic acid, bis-ethyl ester	7.580	177 [M-C_2H_5O]$^+$	149(10)[-C_2H_4]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
	Fluorene	7.621	165 [M-1]	139(30) [-C_2H_2]	165 [M-1]	115(30) [-C_4H_2]
4	Phthalic acid, bis-propyl ester	9.660	191 [M-C_3H_7O]$^+$	149(10) [-C_3H_6]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
	Benzoic acid-benzyl ester	9.662	212 [M]	165(30) [-CH_3O_2][16]	105 [C_7H_5O]$^+$	77(15) [-CO]
5	Phenanthrene-d_{10} (SS)	9.875	188	184(30)	188	159(30)
	Phenanthrene	9.921	178 [M]	150(30) [-C_2H_4]	178 [M]	128(40) [-C_4H_{12}]
	Anthracene	10.198	178 [M]	150(30) [-C_2H_4]	178 [M]	128(40) [-C_4H_{12}]
6	Phthalic acid, bis-iso-butyl ester	10.596	223 [M-C_4H_7]$^+$	149(10) [-$C_4H_{10}O$]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
7	Phthalic acid, bis-butyl ester	11.428	223 [M-C_4H_7]$^+$	149(10) [-$C_4H_{10}O$]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
8	Phthalic acid, bis-methyl-glycol ester	11.766	176 [M-$C_4H_{10}O_3$]$^+$ 104 [M-C7H14O5]$^+$	149(10) [-C_2H_3] 76(10) [-CO]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
9	Phthalicacid bis-4-methyl-2-pentyl ester	12.295	167 [M-$C_{12}H_{23}$]$^+$	149(10) [-H_2O]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
	Fluoranthene	12.337	202 [M]	200(30) [-H_2]	202 [M]	150(50) [-C_4H_4]
10	Phthalic acid, bis-2-ethoxyethyl ester	12.622	193 [M-$C_6H_{13}O_2$]$^+$	149(10) [-C2H4O]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
	Pyrene	12.734	202 [M]	200(30) [-H_2]	202 [M]	150(50) [-C_4H_4]
	Phthalic acid, bis-*n*-pentyl ester	12.868	237 [M-C_5H_9]$^+$	149(10) [-$C_5H_{12}O$]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
11	Phthalic acid, bis-hexyl ester	14.087	251 [M-C_6H_{11}]$^+$	149(10) [-$C_6H_{14}O$]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
	Phthalic acid, benzylbutyl ester	14.156	238 [M-C_4H_{10}]$^+$	104(15) [-$C_9H_6O_3$]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
12	Phthalic acid, hexyl-2-ethlhexyl ester	14.650	251 [M-C_8H_{15}]$^+$	149(10) [-H_2O]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
13	Phthalic acid, bis-2-*n*-butoxyethyl ester	14.848	176 [M-$C_{10}H_{22}O_3$]$^+$ 149 [$C_8H_5O_3$]$^+$	149(10) [-$C_6H_{14}O$] 121(10) [-CO]	101 [$C_6H_{13}O$]$^+$	85(5) [-CH_4]
	Benzo [a] anthracene	14.865	228 [M]	226(30) [-H_2]	228 [M]	200(50) [-C_2H_4]
	Chrysene	14.921	228 [M]	226(30) [-H_2]	228 [M]	200(50) [-C_2H_4]
14	Phthalic acid, bis-cyclohexyl ester	15.095	167 [M-$C_{12}H_{23}$]$^+$	149(10) [-H_2O]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
	Phthalic acid, bis-2-ethyhexyl ester	15.161	167 [M-$C_{16}H_{35}$]$^+$	149(10) [-H_2O]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
15	Phthalic acid, bis-nonyl ester	15.721	293 [M-C_9H_{17}]$^+$	149(10) [-$C_9H_{20}O$]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
16	Phthalic acid, bis-1-octyl ester	16.226	279 [M-C_8H_{15}]$^+$	149(10) [-$C_8H_{18}O$]	149 [$C_8H_5O_3$]$^+$	121(10) [-CO]
17	Benzo [b] fluoranthene	16.654	252 [M]	250(30) [-H_2]	252 [M]	224(50) [-C_2H_4]
	Benzo [k] fluoranthene	16.705	252 [M]	250(30) [-H_2]	252 [M]	224(50) [-C_2H_4]
18	Benzo [a] pyrene	17.253	252 [M]	250(30) [-H_2]	252 [M]	224(50) [-C_2H_4]
	Pyrene-d_{12} (SS)	17.523	264	263(10)	264	236(30)
19	Indeno [1,2,3-cd] pyrene	18.944	276 [M]	274(40) [-H_2]	276 [M]	249(50) [-C_2H_3]
	Dibenzo [a,h] anthracene	19.162	276 [M]	274(40) [-H_2]	276 [M]	249(50) [-C_2H_3]
	Benzo [g,h,i] perylene	19.332	278 [M]	275(40) [-H_3]	278 [M]	250(50) [-C_2H_2]

16 native PAHs and three deuterium PAHs in methanol–methylene chloride was purchased from Supelco (Bellefonte, PA). The standard mixture of 17 PAEs in *n*-hexane was purchased from Dr. Ehrenstorfer. Dipropyl phthalate in cyclohexane was purchased from Dr. Ehrenstorfer. These solutions were used as spiking and calibration solution. Clean soil No. 3 was purchased from R.T. Corporation (Laramie, WY). Reference material IRM 104A was purchased from Ultra Scientific (North Kingstown, RI) and used for recovery studies.

Apparatus

A Varian 320 triple quadrupole mass spectrometer (mass range from *m/z* 10 to 2000) was coupled to the gas chromatograph Varian 3800 (Palo Alto, CA). A deactivated fused-silica capillary column (5 m × 0.25 mm i.d.) from Agilent (Santa Clara, CA) was used as guard column connected to Varian Factor-Four VF-5ht analytical capillary column (30 m × 0.25 mm i.d. × 0.1-µm film thickness).

MAE was performed with a MARS-5 microwave accelerated reaction system for extraction (CEM, Matthews, NC).

Soil sampling

At each field, topsoil samples (depth 0–20 cm) were collected with a spade. Soil samples were transported and stored under 4°C in pre-cleaned glass containers.

Extraction procedure and clean-up steps

The clean soil and reference material were stored in refrigeration until analysis (T ≤ 4°C). Samples for recovery studies were spiked with the corresponding volume of working solutions. Ten grams of soil sample were weighed. Next, 2.0 g of florisil (Sigma Aldrich, St. Louis, MO, 60–100 mesh), previously baked at 600°C for 4 h, was added. The sample was triturated in a glass mortar. All of the glassware was prepared in the following order: soaked in 5% $K_2Cr_2O_4$ sulfuric acid solution overnight, washed with water and distilled water, dried in an oven, then rinsed with acetone and *n*-hexane just before use (10). The aforementioned mixture was transferred into glass vessel (MAE). The solvent used for extraction was 20 mL dichloromethane–acetone (1:1, v/v) (11). The operational parameters of the MARS-5 apparatus applied were: 1200 w, magnetron power 100%; time to reach settings 10 min; extraction temperature 120°C; extraction duration 10 min. Baked and ground anhydrous Na_2SO_4 was used to remove moisture from the extraction. A six-milliliter glass cartridge with 1 g florisil (Supelco) was used for SPE. After concentrating the extract to 2 mL, the solvent was changed from dichloromethane–acetone to hexane to decrease the polarity of the solvent. The elution of the cartridges was performed at a flow rate of 2 mL/min. The final extract was centrifuge at 8000 rpm/min for 10 min, then evaporated to near dryness with a nitrogen stream, and redissolved with *n*-hexane to 1.0 mL.

Table II. Analytical Result of the Reference Material IRM 104A*

Compund	Mean Value (mg/kg)	RSD (%)	RV* (mg/kg)	CI* (mg/kg)
Phthalic acid, bis-ethyl ester	5.40	17.80	6.25	5.66–6.85
Phthalic acid, bis-butyl ester	0.48	16.85	0.465	0.423–0.508
Phthalic acid, benzylbutyl ester	0.45	14.32	0.491	0.448–0.533
Phthalic acid, bis-2-ethyhexyl ester	1.46	5.53	1.34	1.24–1.45
Phthalic acid, bis-1-octyl ester	0.67	9.96	0.764	0.691–0.836
Naphthalene	0.60	18.49	0.565	0.513–0.617
Acenaphthene	0.51	17.00	0.544	0.501–0.587
Fluorene	0.43	13.22	0.626	0.58–0.673
Phenanthrene	4.40	13.30	4.66	4.36–4.96
Anthracene	0.26	10.54	0.365	0.326–0.404
Fluoranthene	8.39	14.91	9.2	8.58–9.82
Pyrene	5.92	10.74	7.43	6.88–7.97
Benzo [a] anthracene	3.45	9.18	5.41	5.01–5.82
Chrysene	6.41	11.21	6.59	6.14–7.05
Benzo [b] fluoranthene	5.56	9.45	5.22	4.86–5.58
Benzo [k] fluoranthene	3.18	11.47	3.49	3.22–3.76
Benzo [a] pyrene	0.36	8.47	0.396	0.340–0.452
Dibenzo [a,h] anthracene	1.27	15.43	1.08	0.99–1.17
Benzo [g,h,i] perylene	0.41	9.68	0.378	0.341–0.416

* RV = reference value; CI = confidence interval

GC–QqQ-MS–MS analysis

One microliter of the final extract was injected into the chromatographic system. The temperature of the injector was set at 310°C. The initial split ratio was 20:1. While injecting the sample, the split ratio was shut off. Then the split ratio was 100:1 at 3.5 min and 20:1 at 10 min. The chromatographic oven temperature program was as follows: the initial temperature of 60°C was held for 2 min after injection. Then it was increased up to 160°C at 30°C/min (hold for 3.0 min), to 270°C at 15°C/min (hold for 1.0 min), to 300°C at 15°C/min (hold for 1.0 min), to 320°C at 20°C/min (hold for 1.0 min). Helium (99.999%) at a constant flow rate of 1.0 mL/min was used as carrier gas; argon (99.99%) at a pressure of 1.80 mTorr was used as collision gas. The running time was of 21.67 min, divided into 19 segments. The QqQ mass spectrometer was carried out under the following conditions: ionization with electron impact at 70 eV in MRM. The transfer line, manifold, and ionization source temperatures were set at 320, 40, and 300°C, respectively. A filament multiplier delay of 4.0 min was fixed in order to prevent instrument damages. The electron multiplier voltage was set at 1200 V. The dwell time was 0.05 s. Peak widths of *m/z* 3.0 and 2.0 were set in the first (Q1) and third quadrupole (Q3), respectively.

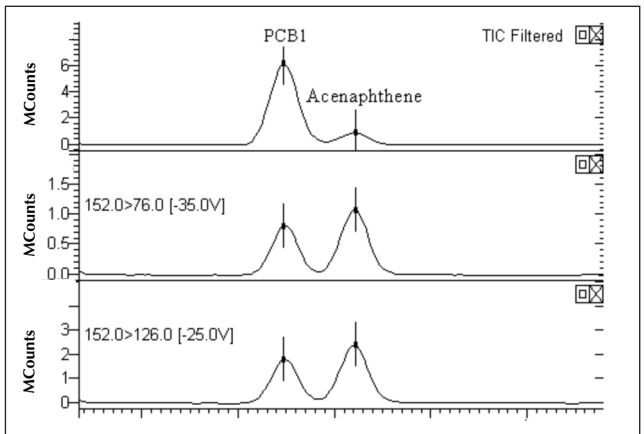

Figure 1. Total ion chromatogram and MRM chromatogram of PCB1 and acenaphthene.

Results and Discussion

Optimization of sample pretreatment steps

At present, PAEs are ubiquitous environmental pollutants. Interferences are easily introduced during the pretreatment steps, especially phthalic acid bis-iso-butyl ester, phthalic acid bis-butyl ester, and phthalic acid bis-2-ethyhexyl ester. Organic solvents and N_2 were main sources, which may cause detection of PAEs in full procedure blanks. Distilling organic solvents with $KMnO_4$ and clean-up N_2 with hydrocarbon trap can solve this problem. In the last few years, new extraction techniques have been established, such as MAE, supercritical fluid extraction (SFE), and accelerated solvent extraction (ASE). MAE offers greatly reduced usage of organic solvents and extraction times. In addition, the glass or PTFE vessel of MAE can avoid the introduction of PAEs to the utmost extent. So MAE with glass vessel was used in this study. And glass SPE cartridge was chose for the same purpose.

The optimization of the cleanup steps was performed with blank soil samples spiked at 5 µg/kg. Among the many purification protocols, SPE (12,13) is one of the most popular purification methods. Different ratios of Hex–Ace (9:1, 4:1, 3:2) were tested for cleanup. Increasing the polarity of the solvent resulted in better recovery. But a great decrease of QqQ's sensitivity was observed when the ratio 3:2 was applied due to the higher matrix content in the final extract. A compromise solution was chosen with an elution solvent mixture Hex–Ace (4:1, v/v), which provided recoveries in the range of 66.59–122.07% at 5 µg/kg.

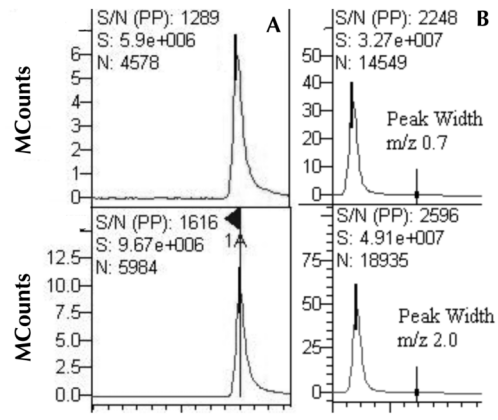

Figure 2. The S/N compared between peak width *m/z* 0.7 and peak width *m/z* 2.0 in third quadrupole (Q3) of phthalic acid, (A) bis-methyl ester and (B) anthracene. For phthalic acid, bis-methyl ester, the S/N enhanced 25%. For anthracene, the S/N enhanced 15%.

GC–QqQ-MS–MS analysis

Optimization of the GC conditions

Sometimes the chromatographic separation is not a critical stage in the development of a multi-residue method with QqQ analyzers as the high QqQ acquisition speed permits the possibility of monitoring co-eluted compounds with a high number of transitions simultaneously in MRM (14). But for isomeric compounds or the compounds with similar structure, the chromatographic separation is important due to the same precursor ions and product ions. In this study, if GC temperature program is not optimized, co-elution of PCB 1 and acenaphthene would affect the qualitative and quantitative analysis of acenaphthene. The ion *m/z* 152 of PCB 1 can produce the ion *m/z* 126 and 76 as acenaphthene, and the proportions of the abundance between *m/z* 126 and 76 are very similar too (Figure 1). The final program can separate 37 compounds (including 16 PAHs, 18 PAEs, one internal standard, and two surrogate standards) in 21.67 min.

Optimization of the MS–MS conditions

In the optimization of the MS–MS conditions, full-scan spectra were obtained to select the precursor ions (Table I). Then, product ion spectra were acquired by collision-induced dissociation (CID) with argon. Collision energies (CEs) from 0 to 50 eV were applied. The aforementioned criterion was also applied to choose the most suitable product ions. The final purpose was to develop a MRM method with two or three reactions or transitions per compound. The preferred precursor ions were the ions with the highest *m/z* ratio (increase in selectivity) and abundance (increase in sensitivity). Furthermore the signal-to-noise ratio (S/N) of the product ions must be considered. Broadening the peak width moderately can make for better sensitivity. P. Plaza Bolanos set peak width in the third quadrupole (Q3) at *m/z* 1.5 (14). In our study, we found that the S/N

Table III. Incidence of PAEs and PAHs in Soil Samples

Compund	N*	Mean (µg/kg)	Min–Max† (µg/kg)	Compund	N*	Mean (µg/kg)	Min–Max† (µg/kg)
PA‡, bis-methyl ester	19	4.01	ND§–14.10	Naphthalene	20	4.44	0.81–8.39
PA, bis-ethyl ester	20	9.25	1.11–27.10	Acenaphthene	13	0.49	ND–2.40
PA, bis-propyl ester	0	ND	ND	Acenaphthylene	8	0.89	ND–2.17
Benzoic acid-benzyl ester	4	3.03	ND–4.98	Fluorene	19	2.57	ND–6.52
PA, bis-iso-butyl ester	20	139.53	8.9–334.91	Phenanthrene	20	8.88	1.17–25.03
PA, bis-butyl ester	20	61.21	2.41–145.51	Anthracene	12	0.65	ND–7.61
PA, bis-methylglycol ester	0	ND	ND	Fluoranthene	20	2.04	0.40–4.34
PA, bis-4-methyl-2-pentyl ester	0	ND	ND	Pyrene	20	0.81	0.17–1.46
PA, bis-2-ethoxyethyl ester	0	ND	ND	Benzo [a] anthracene	16	0.54	ND–1.77
PA, bis-*n*-pentyl ester	10	1.15	ND–3.14	Chrysene	20	3.45	0.43–18.37
PA, bis-hexyl ester	2	0.62	ND–0.77	Benzo [b] fluoranthene	20	4.94	1.65–31.39
PA, benzylbutyl ester	0	ND	ND	Benzo [k] fluoranthene	14	0.42	ND–1.20
PA, hexyl-2-ethlhexyl ester	0	ND	ND	Benzo [a] pyrene	20	0.61	0.17–3.08
PA, bis-2-*n*-butoxyethyl ester	0	ND	ND	Indeno [1,2,3-cd] pyrene	20	1.40	0.35–6.25
PA, bis-cyclohexyl ester	0	ND	ND	Dibenzo [a,h] anthracene	10	0.34	ND–3.98
PA, bis-2-ethyhexyl ester	19	173.41	ND–429.56	Benzo [g,h,i] perylene	20	0.57	0.18–2.29
PA, bis-nonyl ester	0	ND	ND				
PA, bis-1-octyl ester	0	ND	ND				

* Number of samples that the residue was detected. † Min–Max: minimum and maximum residue levels found.
‡ PA = Phthalic acid. § Not detected.

could be enhanced more than 15% while setting peak widths in the third quadrupole (Q3) at *m/z* 2.0 to *m/z* 0.7 (Figure 2). As for phthalic acid bis-2-*n*-butoxyethyl ester, the precursor ion with highest abundance was *m/z* 149, then *m/z* 101, and *m/z* 176. But the S/N of product ion *m/z* 121 from *m/z* 149 was lower than that from other two precursor ions (Figure 3). Finally, *m/z* 149 from *m/z* 176 was chose for quantification. After optimizating, the specific MRM conditions are shown in Table I.

Some fragmentation patterns of PAHs and PAEs can be found. After CID with argon, the product ions of PAHs with better abundant were [M-H_2] or [M-C_2H_2]. The fragmentation pattern for most phthalates are very similar. The mass spectrum of phthalic acid, bis-2-ethyhexyl ester, is shown in Figure 4. The main product ion from *m/z* 149 was *m/z* 121, resulting from fragmentation with loss of the aldehyde group with CE 10eV. Besides the most abundant ion at *m/z* 149, the MS spectrum is rather poor. The molecular ion (*m/z* 390) is not detected. The second most important ion is at *m/z* 167. This ion *m/z* 149 from *m/z* 167 results from fragmentation by loss of water. A similar fragmentation pattern is found for the other phthalates.

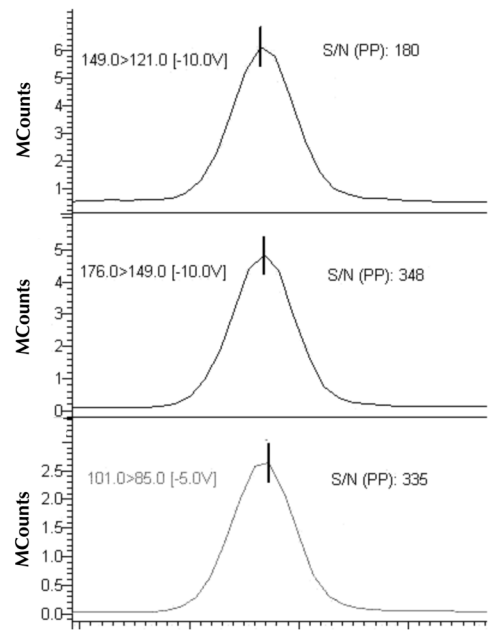

Figure 3. MRM chromatogram of three product ions from phthalic acid bis-2-*n*-butoxyethyl ester.

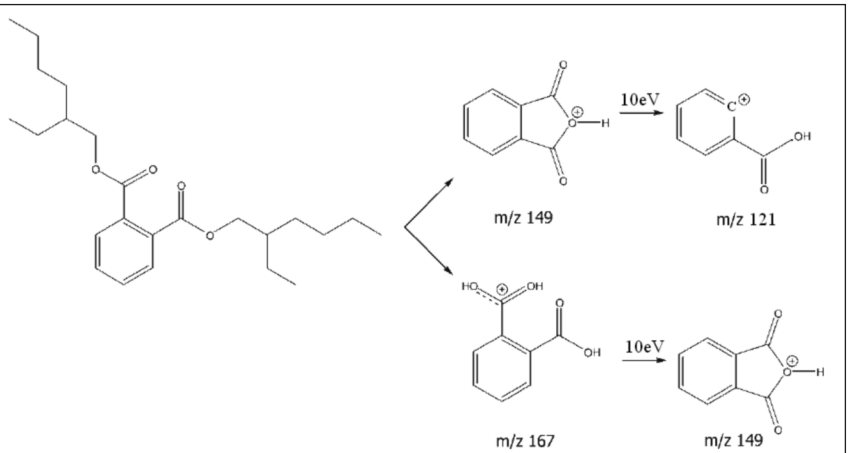

Figure 4. Mass fragmentation of phthalic acid, bis-2-ethoxyethyl ester, in MS–MS mode.

Identification and confirmation of the target compounds

For QqQ-MS methodology, compounds were identified as the target compounds, only when the chromatographic peaks obtained satisfied all of the following criteria (1). The RTW was defined as the retention time (t_R) average plus or minus three standard deviations (SD) of the t_R ($t_R \pm 3SD$) when six blank samples spiked at the second level of calibration were injected (2). The FIT of the spectral match from the sample spectrum to the reference spectrum must be ≥ 850 (arbitrary units, a.u.) (3). The S/N ratio of the target analytes must be >3 for a sample extract. Confirmation was carried out by comparing the sample spectrum with a reference spectrum. Comparison was performed with a forward search which compared the sample spectrum (product ions obtained) with the reference spectrum. The result of this comparison gave a value ranging from 1 to 1000 (arbitrary units, a.u.), which was named FIT by the software. In general, a FIT ≥ 700 (a.u.) confirmed a positive result.

Analytical performance

After optimization of the cleanup procedure and analysis program, precision, linearity, limits of detection (LODs), limits of quantification (LOQs), and confirmation criteria were established. In this work, naphthalene-d_8 was used as internal standard (IS) for PAEs and PAHs. Phenanthrene-d_{10} and pyrene-d_{12} were used as surrogate standards (SS). The coefficient of determination (R^2) values between 0.9920–0.9998 were obtained for all the target compounds from 1 µg/L to 500 µg/L.

One of the main problems in trace analysis of complex matrices is the suppression/enhancement matrix effect. In this work, precision and accuracy were studied using blank samples spiked with standards and reference material IRM 104. All experiments were performed in quintuplicate. In general, recoveries were in the range of 66.59–122.07% while spiked at 5 µg/kg. Among those compounds, the recoveries of phthalic acid bis-mehyl ester, phthalic acid bis-ethyl ester, and some low molecular weight PAHs were slightly lower (between 66.59–83.89%), probably due to their volatility. The possible interferences are the PAEs because they might be introduced easily during the pretreatment steps. In this case, through optimization of sample pretreatment steps, the recoveries of PAEs were controlled satisfactorily within 122.07%. In IRM 104A, the level of PAHs and PAEs were from 0.365 to 9.2 mg/kg, 0.465 to 6.25 mg/kg, respectively. Recoveries were in the range of 63.7–117.6% (Table II). And the average values can match their confidence interval for the majority of compounds. Precision was expressed as relative standard deviation (RSD). RSD were better than 20%

for all of the compounds in this study. LODs and LOQs were calculated in blank soil extracts as the lowest analyte concentration that yielded a S/N ratio of 3 and 10, respectively. In the case of PAEs, LODs and LOQs were in the range of 0.04–0.84 µg/kg and 0.13–2.81 µg/kg, respectively; whereas for PAHs, LODs ranged from 0.01 to 0.51 µg/kg and LOQs from 0.02 to 1.81 µg/kg.

Application to real samples

Twenty real soil samples were analyzed with the developed method. Each batch of samples was processed together with a full procedure blank, a matrix spike, a duplicate, and a reference sample (IRM 104). Each field sample and QC sample were spiked with surrogates at 5 µg/kg.

As can be seen from Table III, phthalic acid bis-2-ethyhexyl ester was the PAE present at the highest concentrations (with an average concentration of 173.41 µg/kg) in soil samples followed by phthalic acid bis-iso-butyl ester and phthalic acid bis-butyl ester (with an average concentration of 139.53 and 61.21 µg/kg, respectively). This is similar to the result in other reports (10,15). These soil samples were also found to contain the PAEs phthalic acid bis-mehyl ester and phthalic acid bis-ethyl ester, which were present in most of the samples. The other PAEs were either absent or present at much lower levels. On the other hand, the PAHs were present at considerably lower concentrations than the PAEs. But they could be detected in nearly every sample. Phenanthrene was the most concentrated PAH with an average concentration of 8.88 µg/kg.

Conclusions

The practicability of a fast SPE clean-up procedure in combination with GC–QqQ-MS–MS for the simultaneous determination of 16 PAHs and 17 PAEs in soils has been shown in this paper. This method was validated obtaining satisfactory accuracy and precision for most of analytes as well as high sensitivity and selectivity, though in some cases LODs and LOQs were at the ng/kg level. The feasibility of the overall method (sample preparation plus instrumental detection) has been evaluated by analyzing reference material with satisfactory results. Finally, determining the PAHs and PAEs in real soil samples has shown the suitability of the method, which involved smaller amounts of samples and organic solvents. These advantages make the method an effective choice to determine of PAE and PAH residues in soils in routine environmental monitoring. Also, the method could be extended to a wider range of application to other types of sample.

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