Analysis of 18 Polycyclic Aromatic Hydrocarbons in Soil Using the QuEChERS Method

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Key Words

PAH, benzofluoranthenes b, j and k, soil, QuEChERS, TraceGOLD TG-17SilMS

Abstract

The use of QuEChERS dispersive SPE as a simple, fast, and quantitative sample preparation method is demonstrated for the GC-MS analysis of 18 polycyclic aromatic hydrocarbons (PAHs) in soil. The suitability of the Thermo Scientific™ TraceGOLD™ TG-17SilMS GC column for the separation of 18 PAHs is also shown. The average recoveries for the spiked 18 PAHs in soil at 1 mg/kg were between 85.0% and 106.7% with relative standard deviations between 0.3% and 2.8% using the original QuEChERS methodology.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are some of the most widespread organic pollutants. In addition to occurring naturally in oil, coal, and tar deposits, PAHs are produced by incomplete combustion of fossil fuels and other organic matter. The compounds are of concern because many have been identified as carcinogenic, mutagenic, or teratogenic. Due to these health risks, regulatory agencies, such as the Environmental Protection Agency (EPA), have defined maximum allowable levels of PAHs in the environment. Sensitive analytical methods are essential in the determination of the presence and levels of PAHs.

QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) is a dispersive solid-phase extraction (SPE) technique initially developed for extracting multi-residue pesticides from fruits and vegetables[1]. The technique has now been extended outside of the food safety field to applications such as removing soil matrix from non-pesticide analytes such as PAHs. The advantages of this methodology are speed, ease of execution, minimal solvent requirement, and cost.

The method is:

- Quick – It has high sample throughput. Typically eight samples can be prepared in under 30 min.
- Easy – It requires less handling of extracts than other techniques; i.e., fewer steps are required.

- Cheap – Less sorbent material and less time is needed to process samples compared to other techniques.
- Effective – The simple technique gives high and accurate recovery levels for a range of different compound types.
- Rugged – The method can detect a large number of compounds including non-polar and polar compounds.
- Safe – Unlike other techniques, it does not require the use of any chlorinated solvents. Extraction is typically carried out using acetonitrile, which is both GC and LC compatible.

A sample preparation approach, described in the original QuEChERS procedure [1], was used for extracting 18 PAHs from soil. This is a two-stage process: sample extraction, followed by dispersive SPE.

In the sample extraction stage, the soil sample is sieved to give uniform surface area so that optimal extraction efficiency can be achieved. The soil sample must be at least 80% hydrated for extraction to work; therefore, water must be added to the soil in the extraction tube. This is

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then followed by the addition of acetonitrile and a salt mixture composed of magnesium sulfate and sodium chloride. The salt mixture initiates a phase separation between water and organic solvent and the analytes of interest are extracted into the organic phase. The tube is then capped, shaken vigorously, and centrifuged.

The second stage of the QuEChERS method uses dispersive SPE, which involves transferring a portion of the acetonitrile extract to a clean-up tube containing a combination of sorbents for removal of unwanted sample components. The sorbent combination of magnesium sulfate and PSA (primary & secondary amines) silica in the sample clean-up tube removes interfering components from the matrix, thus reducing matrix effects and improving method robustness.

The extraction of 18 PAHs from soil was demonstrated using the original QuEChERs methodology. Six extractions at 1 mg/kg of 18 PAHs spiked into soil were used for recovery experiments. Separation of 18 PAHs was achieved on a Thermo Scientific TraceGOLD TG-17SilMS GC column. This low-bleed GC column allows for the quantification of critical pairs such as phenanthrene and anthracene. Similarly, it also provides baseline resolution for isobaric PAHs such as benzofluoranthene b, j and k.

Experimental Details

Consumables		Part Number
Column:	TraceGOLD TG-17SilMS, 30 m × 0.25 mm × 0.25 µm	26072-1420
Septum:	BTO, 17 mm	31303211
Liner:	Thermo Scientific™ Splitless FocusLiner™ for 50 mm needle, 5 × 8 × 105 mm	453T2999
Column Ferrules:	100% graphite ferrules for Thermo Scientific™ TRACE™ injector 0.1–0.25 mm ID	29053488
Colum Ferrules:	Graphite/Vespel® for transfer line 0.1–0.25 mm ID	29033496
Injection Syringe:	10 µL fixed needle syringe for Thermo Scientific™ TriPlus RSH™ Autosampler	365D0291
Vials and Closures:	Thermo Scientific 9 mm Wide Opening Screw Thread Vial Convenience Kit, 2 mL Clear Vial with Patch, Blue Polypropylene Closure with Clear PTFE/Blue Silicone Septa	60180-599
Reagents:	Fisher Scientific™ LC-MS grade acetonitrile Fisher Scientific LC-MS grade water	A/0638/17 W/0112/17
QuEChERS Extraction Stage:	Thermo Scientific™ HyperSep™ Dispersive SPE multipacks, 4000 mg magnesium sulfate, and 1000 mg sodium chloride. Each pack contains 50 metalized pouches with 50 empty centrifuge tubes with plug seal caps	60105-332
QuEChERS Dispersive SPE Stage:	Thermo Scientific HyperSep Dispersive SPE clean-up product, 2 mL tube containing 150 mg magnesium sulfate, 50 mg PSA	60105-203

Preparation of Calibration Standards

The calibration curve was constructed with a mixture of 18 PAHs listed in Table 1 at the following concentrations: 50, 100, 200, 500, 1000, and 2000 ng/mL. To each 1 mL of calibration standard solution, 10 µL of 50 µg/mL mixture of internal standards (IS) containing napthalene-d_8, acenapthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} was added.

Internal Standard	Compound
Napthalene-d_8 (IS 1)	Napthalene
Acenapthene-d_{10} (IS 2)	Acenaphthylene, Acenapthene, Fluorene
Phenanthrene-d_{10} (IS 3)	Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene
Chrysene-d_{12} (IS 4)	Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[j]fluoranthene, Benzo[a]pyrene, Benzo[e]pyrene
Perylene-d_{12} (IS 5)	Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthracene, Benzo[g,h,i]perylene

Table 1: PAHs quantified against the internal standards used for calibration and recovery experiments

Sample Preparation

Samples were prepared as described in Figure 1.

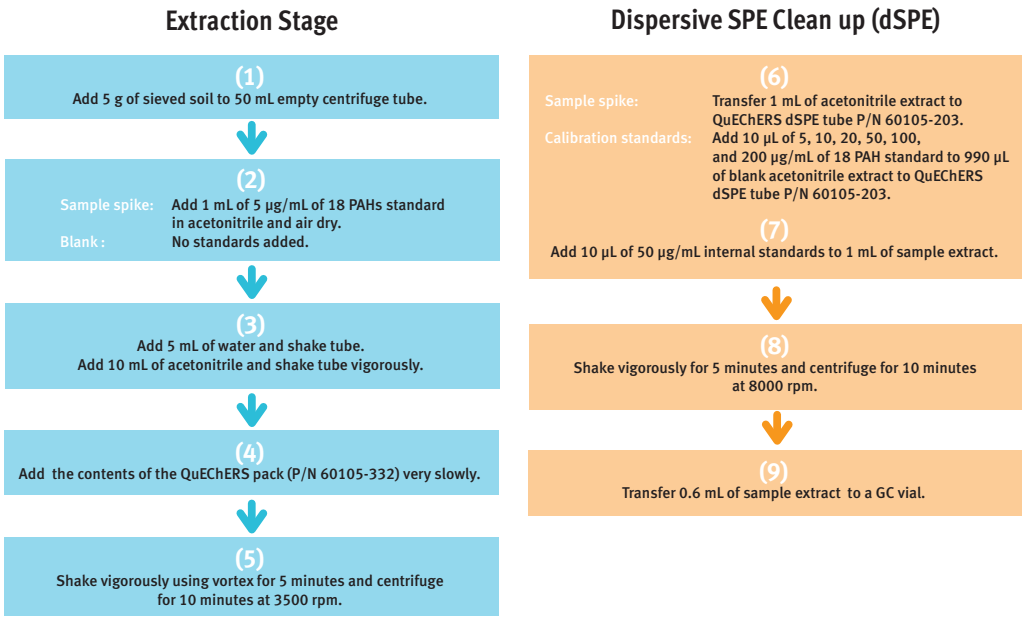

Figure 1: Sample preparation illustrating QuEChERS protocol

Separation Conditions

Instrumentation:	Thermo Scientific TRACE GC Ultra
Carrier Gas:	Helium
Column Flow:	1.2 mL/min, constant flow
Oven Temperature:	90 °C (1.0 min), 30 °C/min, 250 °C, 4 °C/min, 330 °C (5 min)
Injector Type:	Split/Splitless
Injector Mode:	Split 25:1, 30 mL/min split flow
Injector Temperature:	250 °C
Detector Type:	Thermo Scientific™ ISQ™ mass spectrometer
Transfer Line Temperature:	300 °C
Source Temperature:	250 °C
Ionization Conditions:	EI
Electron Energy:	70 eV
SIM Scan Parameters:	Table 2

Scan window start time (min)	Compound	*m/z* Quan ion	Dwell time (sec)
3.00	Napthalene, Naphthalene-d_8	128, 136	0.12
4.80	Acenaphthylene, Acenaphthene, Acenaphthene-d_{10}	152, 154, 164	0.10
5.90	Fluorene	166	0.25
6.60	Phenanthrene, Anthracene, Phenanthrene-d_{10}	178, 188	0.12
8.10	Fluoranthene, Pyrene	202	0.25
11.40	Benz[a]anthracene, Chrysene, Chrysene-d_{12}	228, 240	0.12
15.50	Benzo[b]-, Benzo[j]-, Benzo[k]fluoranthene, Benzo[a]-, Benzo[e]pyrene	252	0.25
19.55	Perylene-d_{12}	264	0.25
22.00	Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene	276, 278	0.12
24.80	Benzo[g,h,i]perylene	276	0.25

Table 2: SIM scan parameters

Injection Conditions	
Instrumentation:	Thermo Scientific TriPlus RSH Autosampler
Injection Volume:	1 µL
Pre- and Post-Injection Dwell Time:	1.0 s

Data Processing	
Software:	Thermo Scientific™ XCalibur™

Results

The separation of the 18 PAHs was obtained using a low bleed TraceGOLD TG-17SilMS GC column. The analysis was performed in SIM mode. Figure 2 shows the SIM chromatogram of spiked PAHs in soil matrix at 1 mg/kg level.

To assess the method linearity, a calibration curve was constructed for each of the PAHs using the appropriate internal standard (Table 1), The coefficients of determination (R^2) between area ratio of sample and internal standard for 18 PAHs were >0.997 (Table 3), demonstrating excellent method linearity.

Six extractions of spiked samples at 1 mg/kg were carried out and recoveries and reproducibility (RSD) measured. Table 3 shows the recoveries and RSDs for the spiked 18 PAHs in soil, which were between 85.0% and 106.7%, with RSDs between 0.3% and 2.8%.

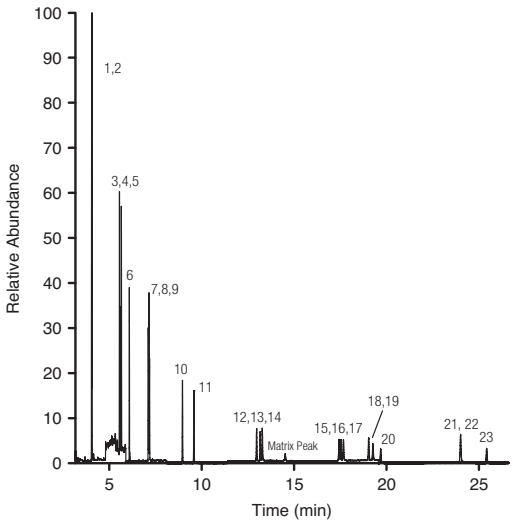

Figure 2a: SIM chromatogram of 18 PAHs in soil matrix solution at 500 ng/mL

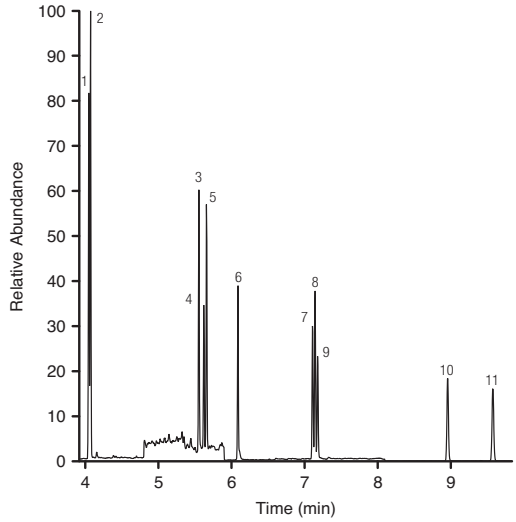

Figure 2b: Expanded SIM chromatogram of 18 PAHs in soil matrix solution at 500 ng/mL

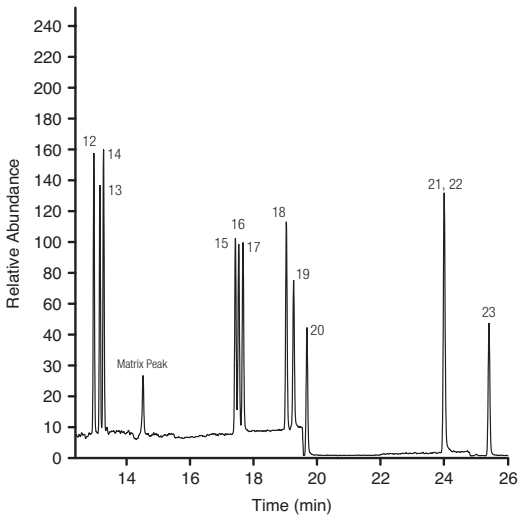

Figure 2c: Expanded SIM chromatogram of 18 PAHs in soil matrix solution at 500 ng/mL

Peak	Compound	t_R (min)	Linearity (R^2)	% Recovery (n=6)	%RSD (n=6)
1	Napthalene-d_8 (IS 1)	4.06	-	-	-
2	Napthalene	4.08	0.9974	85.0	0.6
3	Acenaphthylene	5.56	0.9988	98.2	1.1
4	Acenapthene-d_{10} (IS 2)	5.63	-	-	-
5	Acenapthene	5.66	0.9992	96.3	0.8
6	Fluorene	6.09	0.9991	100.2	1.1
7	Phenanthrene-d_{10} (IS 3)	7.14	-	-	-
8	Phenanthrene	7.15	0.9992	98.6	0.5
9	Anthracene	7.18	0.9992	96.7	0.3
10	Fluoranthene	8.98	0.9985	105.6	1.2
11	Pyrene	9.58	0.9986	106.7	1.0
12	Benzo[a]anthracene	12.98	0.9990	99.3	0.4
13	Chrysene-d_{12} (IS 4)	13.16	-	-	-
14	Chrysene	13.27	0.9993	96.9	0.5
15	Benzo[b]fluoranthene	17.42	0.9993	93.1	0.6
16	Benzo[k]fluoranthene	17.54	0.9990	93.1	0.6
17	Benzo[j]fluoranthene	17.70	0.9993	97.4	0.4
18	Benzo[a]pyrene	19.03	0.9990	88.7	0.4
19	Benzo[e]pyrene	19.25	0.9994	87.1	0.8
20	Perylene-d_{12} (IS 5)	19.77	-	-	-
21	Indeno[1,2,3-cd]pyrene	24.00	0.9993	91.7	2.2
22	Dibenzo[a,h]anthracene	24.00	0.9993	95.8	2.8
23	Benzo[g,h,i]perylene	25.40	0.9990	90.8	1.2

Table 3: Peak identification, linearity and recovery data for 18 PAHs in soil spiked at 1 mg/kg

Conclusion

The QuEChERS sample preparation method provided a fast and simple approach for extracting and analyzing 18 PAHs in soil achieving high recoveries and excellent reproducibility. The QuEChERS – GC-MS method was found to be linear in the concentration range of 50 to 2000 ng/g. The TraceGOLD TG-17SilMS GC column provided good chromatographic separation for all analytes studied.

References

1. M. Anastassiades, S.J. Lehotay, D. Stajnbaher and F.J. Schenck, J AOAC Int 86 (2003) 412.

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