

Determinación de los PAH (EU15+1) en suelos mediante una solución automatizada QuEChERS

Aplicación 029

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RESUMEN

Los Hidrocarburos Policíclicos Aromáticos (PAH) constituyen un conjunto de compuestos que pueden encontrarse en el medio ambiente. Estos compuestos están controlados tanto por la agencia europea como por la “US Environmental Protection Agency” dado su carácter cancerígeno y son objeto de preocupación desde 1980.

El Método de extracción QuEChERS (Quick-Easy-Cheap-Effective-Rugged-Safe) fue desarrollado para la determinación de residuos de pesticidas en productos agrícolas en 2003, el método QuEChERS puede adaptarse a muchas matrices como pueda ser el análisis de PAH en suelos.

La presente aplicación valida el método de extracción automatizado mediante el sistema AutoMate-Q40 para el análisis de PAH en suelo. Los compuestos se determinan mediante espectrometría gases-masas (GC-MS) monitorización selectiva de ion (SIM).

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are chemical compounds that consist of fused aromatic rings. PAHs exist naturally in the environment and are also formed by the incomplete burning of carbon containing material such as oil, wood, garbage, coal and fuel. Maximum amounts of PAHs are formed when organic material is burned from 500-700°C¹. These compounds have been identified as carcinogenic and mutagenic from various agencies throughout the world. With these risks, the European Union (EU) and the US Environmental Protection Agency (USEPA) have set maximum allowable limits of PAHs in environmental samples².

The QuEChERS extraction method is applicable for PAHs, since it offers good selectivity and sensitivity when extracting these compounds in soil samples.³ The aim of this project is to evaluate the performance and versatility of the

AutoMate-Q40 for the extraction of PAHs in soil by a modified QuEChERS extraction. Gas Chromatograph coupled to a Mass Spectrometer (GC-MS) was employed for the detection of PAHs in soil. Quantification was based on matrix-matched calibration curves.

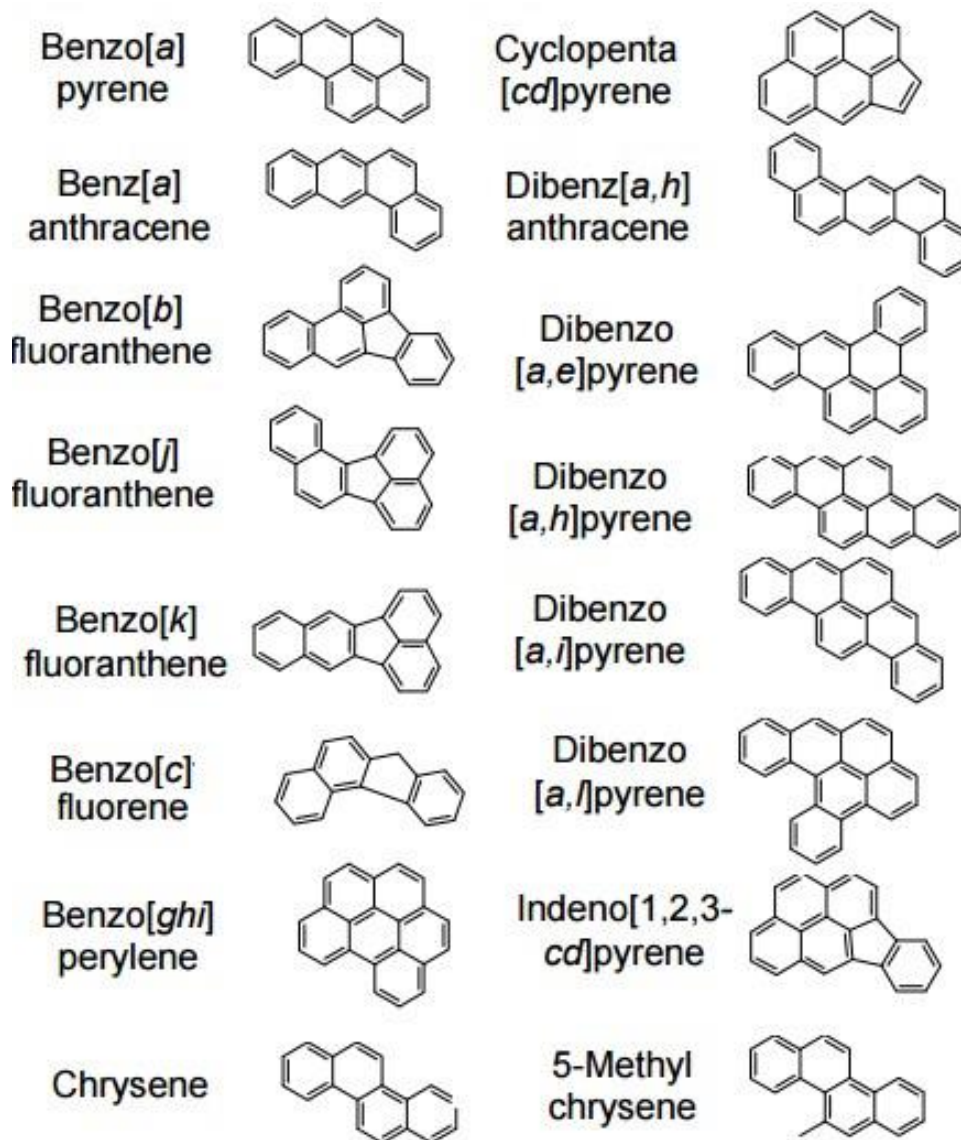


Experimental Instrument Conditions

Chemicals Structures

See Figure 1 for the PAHs used in this study

Figure 1 Polycyclic Aromatic Hydrocarbons (PAHs) Structures³

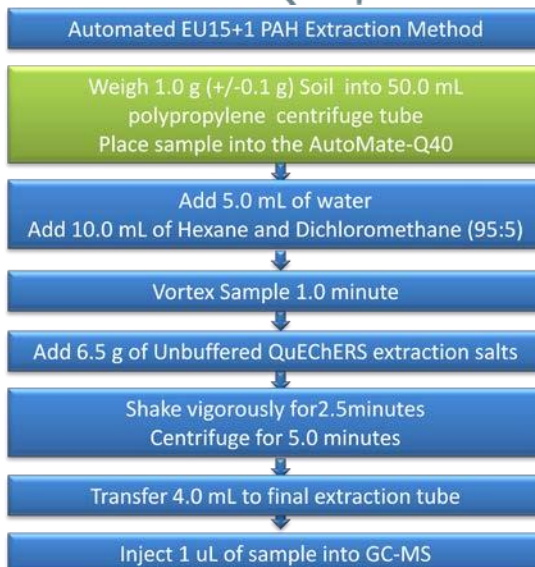


Sample Preparation

Clean soil was purchased from a local hardware store. The soil was placed in the oven to let dry over night. The next day the soil was passed through sieves to give a uniform surface area, so optimal extraction efficiency could be achieved.

For this analysis, the AutoMate-Q40 used 6.5 g of Unbuffered QuEChERS extraction salts (MgSO₄ and NaCl). Figure 2 shows the sample preparation and extraction steps for PAHs from soil.

Figure 2 AutoMate-Q40 : Automated Extraction Parameters for soil

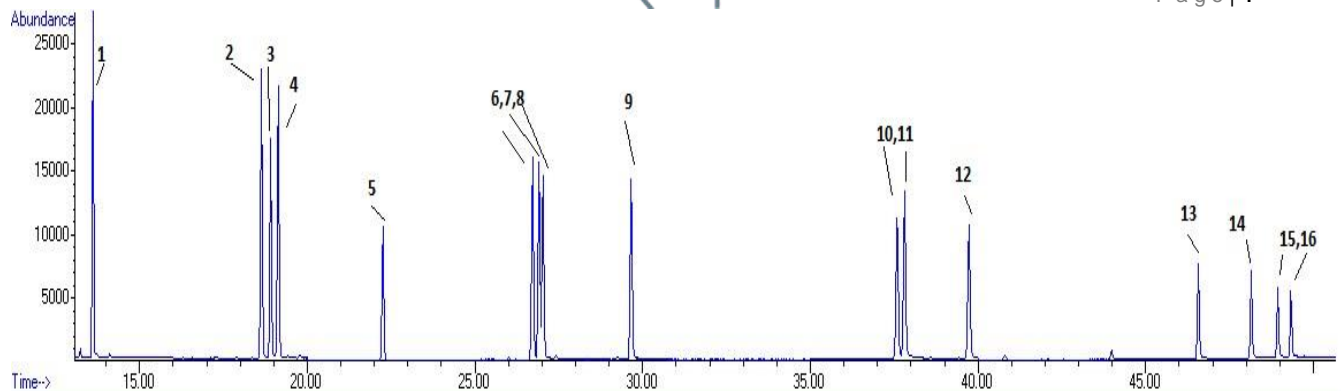


Sample Analysis

Sample analysis was conducted using an Agilent GC/MS system. For separation of the compounds of interest, a Restek Rxi-PAH column was used. Table I demonstrates the optimized GC/MS analysis parameters for both the chromatographic separation and mass selection. Figure 3 shows the SIM GC chromatogram with a spiked PAHs calibration standard.

Table I GC/MS Parameters	
GC Parameters	
Column	Restek Rxi-PAH 40m x 0.18mm x 0.07um
Oven Program	110°C (1.25min) 29°C/min to 210, 2.5° C/min to 295°C, 4.7° C/min to 350° C (4.7min)
Inlet	275 C, 1.01 mL/min helium, Splitless, 40 mL/min Purge Flow
Transfer Line	280°C
MS Parameters	
Mass Range	Selective Ion Monitoring (SIM)
Ion Source	EI, 276 °C

Figure 3 SIM GC chromatogram of a high level PAH calibration standard



1. Benzo[c]fluorine 2. Benz[a]anthracene 3. Cyclopenta[cd]pyrene 4. Chrysene 5. 5-Methylchrysene 6. Benzo[b]fluoranthene 7. Benzo[k]fluoranthene 8. Benzo[j]fluoranthene 9. Benzo[a]pyrene 10. Indeno[1,2,3-cd]pyrene 11. Dibenz[a,h]anthracene 12. Benzo[ghi]perylene 13. Dibenzo[a,l]pyrene 14. Dibenzo[a,e]pyrene 15. Dibenzo[a,i]pyrene 16. Dibenzo[a,h]pyrene

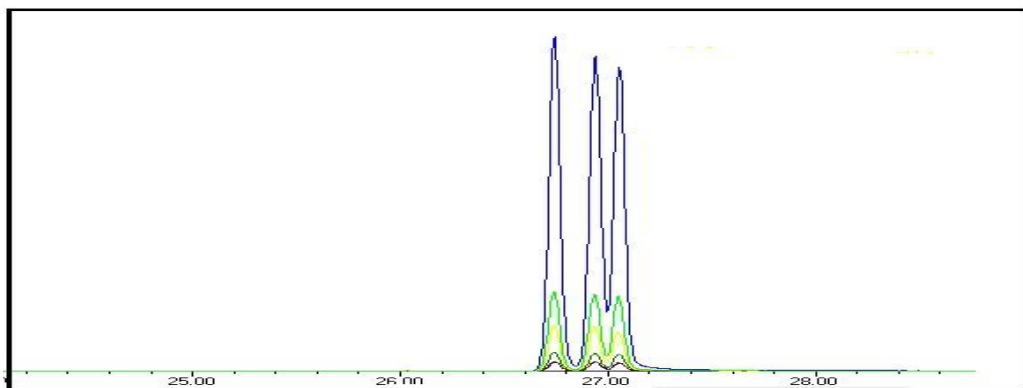
Results

Calibration Results

Calibration standards were prepared from 10-400 µL/L using matrix matched blanks for the soil samples. The correlation coefficients (r^2) are shown in Table II. Figure 4 shows the GC/MS chromatogram separation and overlay for Benzo[b]fluoranthene, Benzo[k]fluoranthene and Benzo[j]fluoranthene.

Calibration Results for EU15+1 PAH	
Compounds	Soil
	Calibration r^2
Benzo[c]fluorene	1.0000
Benz[a]anthracene	0.9998
Cyclopenta[cd]pyrene	0.9999
Chrysene	0.9999
5-Methylchrysene	0.9999
Benzo[b]fluoranthene	0.9996
Benzo[k]fluoranthene	0.9998
Benzo[j]fluoranthene	0.9999
Benzo[a]pyrene	0.9998
Indeno[1,2,3-cd]pyrene	0.9995
Dibenz[a,h]anthracene	0.9991
Benzo[ghi]perylene	0.9997
Dibenzo[a,l]pyrene	0.9998
Dibenzo[a,e]pyrene	0.9994
Dibenzo[a,i]pyrene	0.9984

Figure 4 Chromatographic calibration overlay for Benzo[b]fluoranthene, Benzo[k]fluoranthene and Benzo[j]fluoranthene. Common Isobaric masses m/z 252



Reproducibility and Accuracy Results

Automating the QuEChERS extraction enables an easy, reliable and more reproducible extraction. The AutoMate-Q40 offers significant labor savings, while improving the reproducibility and consistency between samples.

A precision and accuracy study was performed using the AutoMate-Q40. A 2.0 µg/mL stock PAH solution was used to fortify the soil samples. Check standards were fortified at 10.0 and 20.0 µg/L using the AutoMate-Q40's ability to make standard additions. This translates to 0.1 and 0.2 mg/kg in the final sample for soil.

These QC samples were quantified against their corresponding matrix matched calibration. The results for soil can be seen in Tables III. This table also shows that recoveries were between 70.0% and 107.0%, with RSD between 1.5% and 14.3%.

Table III Soil Spike Recovery				
Compound	0.1mg/kg Action level		0.2mg/kg Action level	
	%Recovery	%RSD	%Recovery	%RSD
Benzo[c]fluorene	100.2	2.1	106.4	3.3
Benz[a]anthracene	86.3	1.7	99.0	3.1
Cyclopenta[cd]pyrene	105.2	1.7	107.0	3.1
Chrysene	88.3	1.6	99.5	3.3
5-Methylchrysene	96.4	1.7	104.1	3.0
Benzo[b]fluoranthene	82.4	1.8	95.6	3.3
Benzo[k]fluoranthene	85.9	2.0	96.1	3.1
Benzo[j]fluoranthene	89.0	1.8	96.7	3.2
Benzo[a]pyrene	88.7	1.5	96.5	3.2
Indeno[1,2,3-cd]pyrene	84.4	2.0	90.1	3.2
Dibenzo[a,h]anthracene	70.0	1.6	80.3	2.6
Benzo[ghi]perylene	86.7	1.9	89.7	3.5
Dibenzo[a,l]pyrene	98.6	2.7	89.3	4.4
Dibenzo[a,e]pyrene	92.8	4.2	81.7	4.9

Dibenzo[a,i]pyrene	82.1	14.3	84.4	6.1
Dibenzo[a,h]pyrene	87.5	3.7	80.5	4.9
Average	87.9	2.2	92.2	3.6

Conclusion

This study demonstrates the Automate-Q40's ability to successfully process soil samples for PAHs by the QuEChERS extraction method. By automating the liquid handling, addition of salt/buffers, sample mixing, pipetting, and liquid level sensing using the VialVision, the AutoMate-Q40 frees the scientist from a laborintensive extraction method and exposure to unhealthy chemicals.

The automated extraction process enables an easy, reliable and more reproducible extraction. This enables time and labor savings, while improving consistency and reproducibility of the extraction. The combined PAH spikes recoveries of 90.1%, with an average RSD of 2.90% exceed the requirement outlined for this application. These numbers indicate superb precision and accuracy thus validating the performance of the AutoMate-Q40 to adequately perform the QuEChERS extraction method for soil.

References

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2. <http://www3.epa.gov/epawaste/hazard/wastemin/minimize/factshts/pahs.pdf>
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