



Screening PAHs in Soil Using RTL Database with SampliQ QuEChERS Extraction Kits and Agilent 5975T LTM GC/MS

Application Note

Environmental

Authors

Suli Zhao and Andy Zhai
Agilent Technologies (Shanghai) Co., Ltd.
412 Ying Lun Road
Shanghai 200131
China

Abstract

The analysis of PAHs is important in the environmental and consumer product fields. This application note describes a solution for PAH analysis in a soil matrix using the Agilent 5975T LTM GC/MSD with a retention time locking (RTL) method. The RTL screening library was created and a DRS method configured with the installed DRS software. The solution also includes an effective sample pretreatment procedure. This method is suitable for the Agilent 5975T LTM GC/MSD, a transportable GC/MS that provides simplicity, safety and low chemical reagent costs.



Agilent Technologies

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds that consist of fused aromatic rings and do not carry substituents. PAHs are lipophilic, therefore they mix easily with oil and not water. The higher molecular weight PAH compounds are even less water-soluble and volatile. These properties cause PAHs in the environment to be found primarily in soil, sediment and oily substances. As pollutants they are of concern because some compounds have been identified as carcinogenic. One PAH compound, specifically benzo(a)pyrene, is noted as the first chemical carcinogen discovered. For these reasons, PAHs are not only an environmental concern, but also a concern in food and toys.

The EPA has designated 16 PAH compounds as priority pollutants that are often targeted for measurement in environmental samples. This application note describes one method for fast screening of PAHs in soil using a RTL database and RTL method on a transportable Agilent 5975T LTM GC/MSD. The PAHs RTL database was established and stored with the DRS method. The RTL libraries allow easy peak allocation in the matrix. Targets and confirmation are more reliable using the result screener function, which combines the power of spectral matching and retention time locking matching [1]. The RTL database offers quick, 1-minute screening of PAHs in soil and convenient PAH identification. The sample pretreatment uses the QuEChERS extraction method with the Agilent SampliQ QuEChERS EN Dispersive SPE kits. The QuEChERS method is quick, simple and safe and therefore more suitable for both mobile and field laboratory applications.

Experiment

Reagents and Chemicals

All reagents were analytical or HPLC grade. The (16) PAHs were purchased from Sigma-Aldrich (St. Louis, MO, USA), in addition to a mixture for EPA610. The original EPA610 PAH concentrations ranged from 100 to 2000 µg/mL and diluted accordingly. The water was from a MilliQ system (Milford, Mass, USA).

Equipment and Material

The analysis was performed on an Agilent 5975T LTM GC/MSD equipped with an Agilent 7693 autosampler (Agilent Technologies, Shanghai, P.R.China). RTL software was a function of Agilent MSD ChemStation and DRS (A.04.00, p/n G1716AA) was installed. Separation of the compounds was

achieved on an Agilent J&W HP-5ms LTM column (30 m × 0.25 mm, 0.25 µm). Extraction and cleanup were achieved with an Agilent SampliQ QuEChERS EN Extraction kit (p/n 5982-5650) and a SampliQ QuEChERS EN Dispersive SPE kit (p/n 5982-5156).

Instrument Conditions

Table 1. Instrumentation and Conditions of Analysis

Instrumentation:	
GCMS system:	Agilent 5975T LTM GC/MSD
Inlet:	Split/splitless
Autosampler:	Agilent 7693 automatic liquid sampler
Column:	Agilent J&W LTM HP-5ms, 30 m × 0.25 mm, 0.25 µm
Guard column:	1 m column with same phase as analytical column, connected to the injector.
Experimental conditions:	
Inlet temperature:	280 °C
Injection volume:	1 µL
Injection mode:	Splitless
Carrier gas:	Helium
Head pressure:	20.06 psi, constant pressure mode
Method RT locked to pyrene at 19.38 min	
LTM oven temperature:	70 °C (2 min), 10 °C/min, 300 °C (10 min)
Transfer line temperature:	280 °C
MSD interface:	280 °C
Ion source:	230 °C
Quad temperature:	150 °C
Ionization mode:	EI
Scan mode:	Full scan, 80–350 u
EMV mode:	Gain factor
Gain factor:	1.00
Resulting EM voltage:	1082 V
Solvent delay:	3 min

Sample Preparation

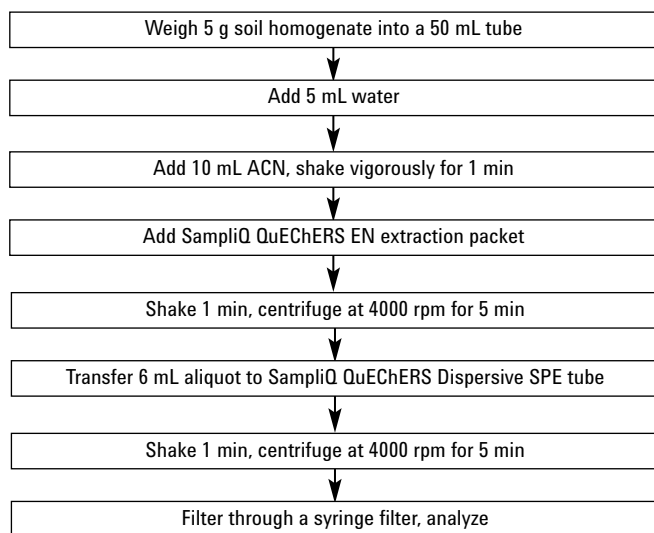
The soil sample was collected from the local garden in Shanghai, China, and pretreated with dichloromethane. It was then air-dried at ambient temperature, and sieved to obtain a homogeneous sample.

Extraction

A 5-g sample of soil homogenate was placed into a 50-mL centrifuge tube. Five mL of water were added to the tube, and the tube shaken vigorously for 1 min. A 10-mL amount of acetonitrile was then added, shaken vigorously for 30 sec, followed by an Agilent SampliQ QuEChERS EN extraction packet, which contained 4 g of anhydrous MgSO₄, 1 g of anhydrous NaCl, 1 g of Sodium Citrate, 0.5 g of disodium citrate sesquihydrate. The sample tubes were hand shaken vigorously for 1 min then further centrifuged at 4000 rpm for 5 min.

Cleanup

A 6.0 mL aliquot of the upper ACN layer was transferred into a SampliQ QuEChERS EN Dispersive SPE 15-mL tube. This tube contained 150 mg of PSA, 150 mg of C18 and 900 mg of anhydrous $MgSO_4$. After one minute of shaking, the tubes were centrifuged at 4000 rpm for 5 min. After a 4-mL aliquot of the extract was filtered through a 0.22 μm filter, (p/n 5064-8222) the sample was ready for analysis.



Results and Discussion

The retention time locking (RTL) software is a function within Agilent MSD ChemStation. The RTL calibration runs are performed automatically. The retention time versus head pressure curve is calculated and stored within the method. The RTL curve sets the locked head pressure relative to the desired target time (for example pyrene, 19.38 min). Once the RTL is set it can be implemented in the method for sample analysis.

This application evaluated the RTL coefficient for the 16 PAHs with the 5975T LTM GC/MSD to assure the reliability of the RTL results. The tested coefficients are between 0.9995 and 0.9999 for the 16 PAHs evaluated.

Pyrene was chosen as the RTL compound based on the following parameters: acceptable retention time, good peak shape, and conformity. These are the requirements for a compound used in the RTL software.

Evaluation of the Locked Method Relative to System Retention Time Repeatability

In order to establish repeatability the analysis method was repeated ten times. All the compounds showed acceptable retention time repeatability and the RT RSD% ranged from 0.002 to 0.037%. RT repeatability is essential to establish a reliable RTL database. Figure 1 illustrates an overlay of the 10 runs to show the retention time repeatability of the entire system.

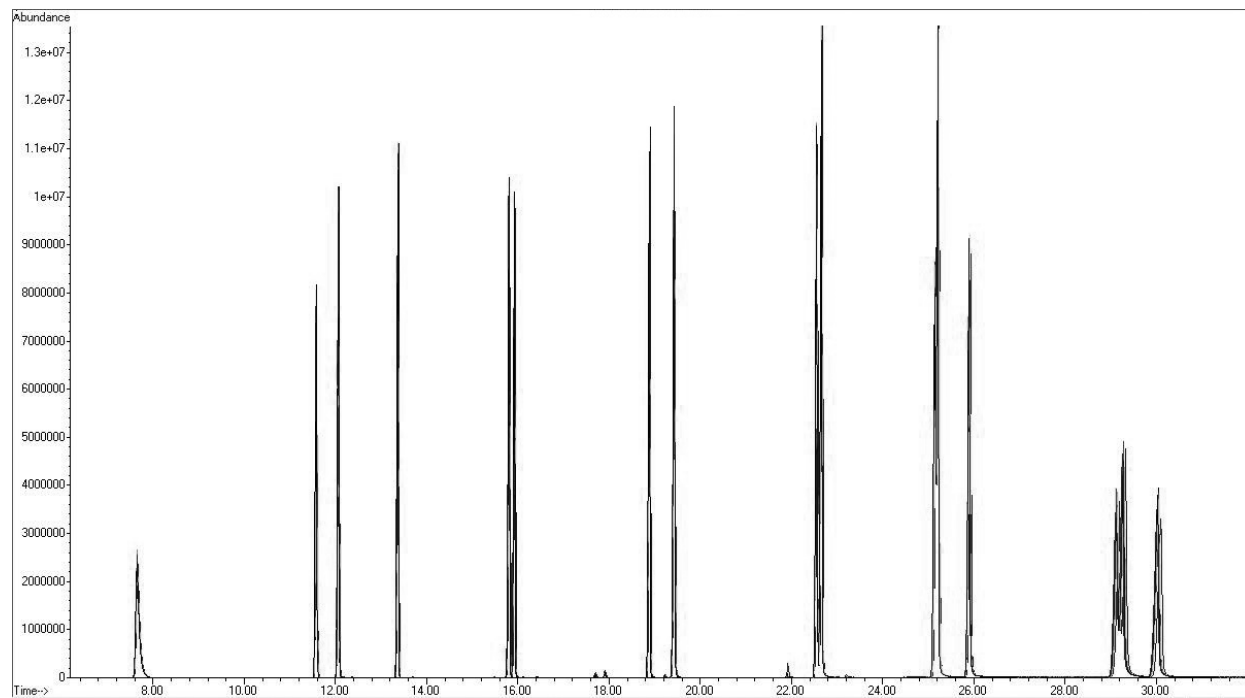


Figure 1. Chromatographic overlay of 10 runs.

Creating the RTL Screening Database Based on the 16 PAH Established Chromatogram

A TIC of the standard with 16 PAHs is shown in Figure 2. The retention time locked screening database is created from the TIC information [2]. Since the database is based upon the retention time and the qualifier ion, this method offers a fast screening of targets from a complicated matrix.

Evaluation of the PAHs in Soil using PAHs RTL Screening Database

The blank soil chromatographs are shown in Figure 3. Illustrations that the QuEChERS method for the pretreatment

soil provides cleaner chromatograms, especially for the late eluters. In general, the later-eluted PAHs often show poor sensitivity, therefore requiring a cleaner matrix. The overlay of the blank soil with and without QuEChERS pretreatment are shown in Figure 3. The cleanliness of the soil background allows accurate determination of the high molecular weight (MW) PAHs.

QuEChERS Pretreatment

The RTL database offers an accurate determination of the target peak retention time to help screen for PAHs in a soil matrix. Figure 4 shows a chromatogram of 16 PAHs added in a soil matrix.

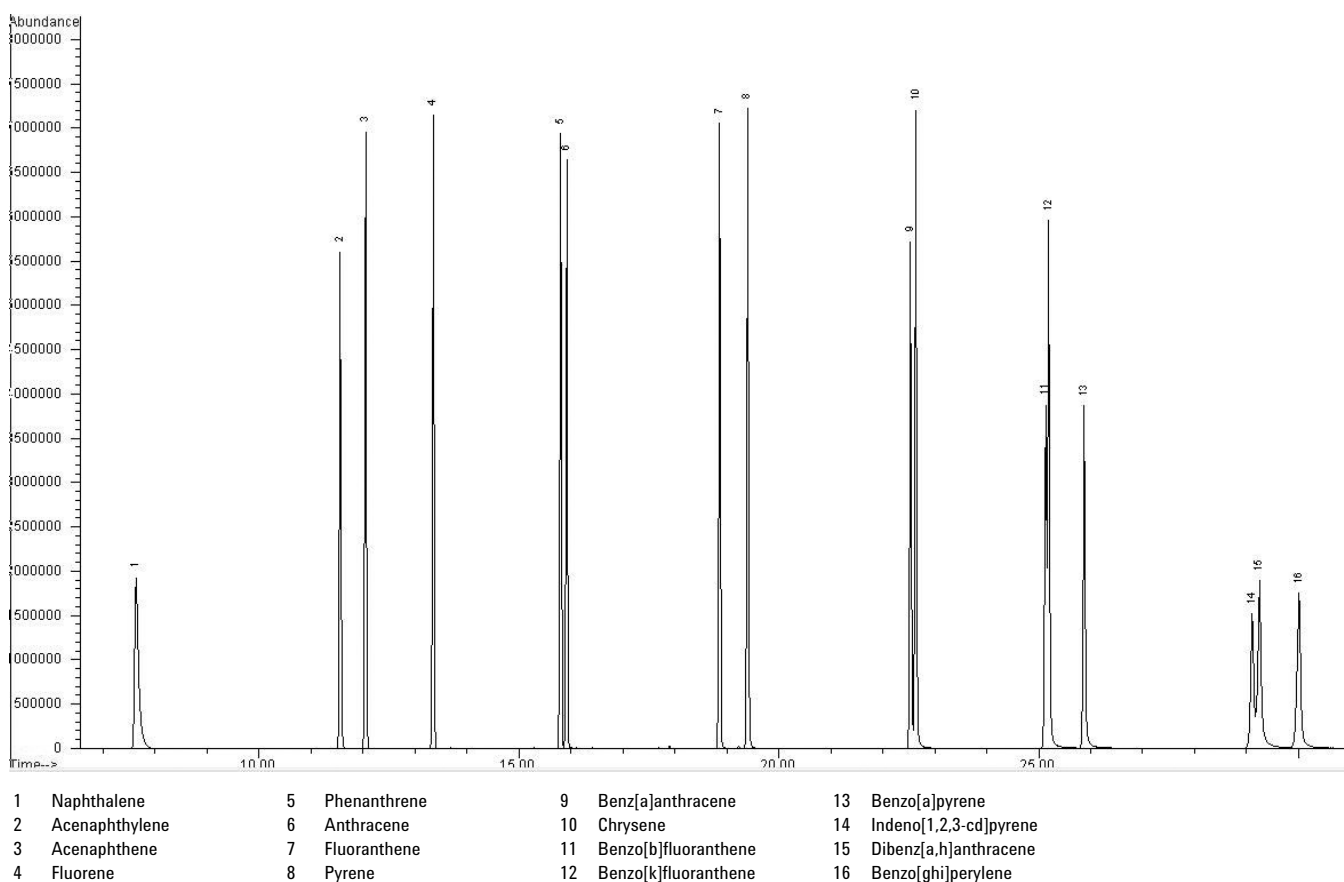


Figure 2. Total ion chromatogram (TIC) of 16 PAHs in a standard mixture. The concentration was 2.0 µg/mL.

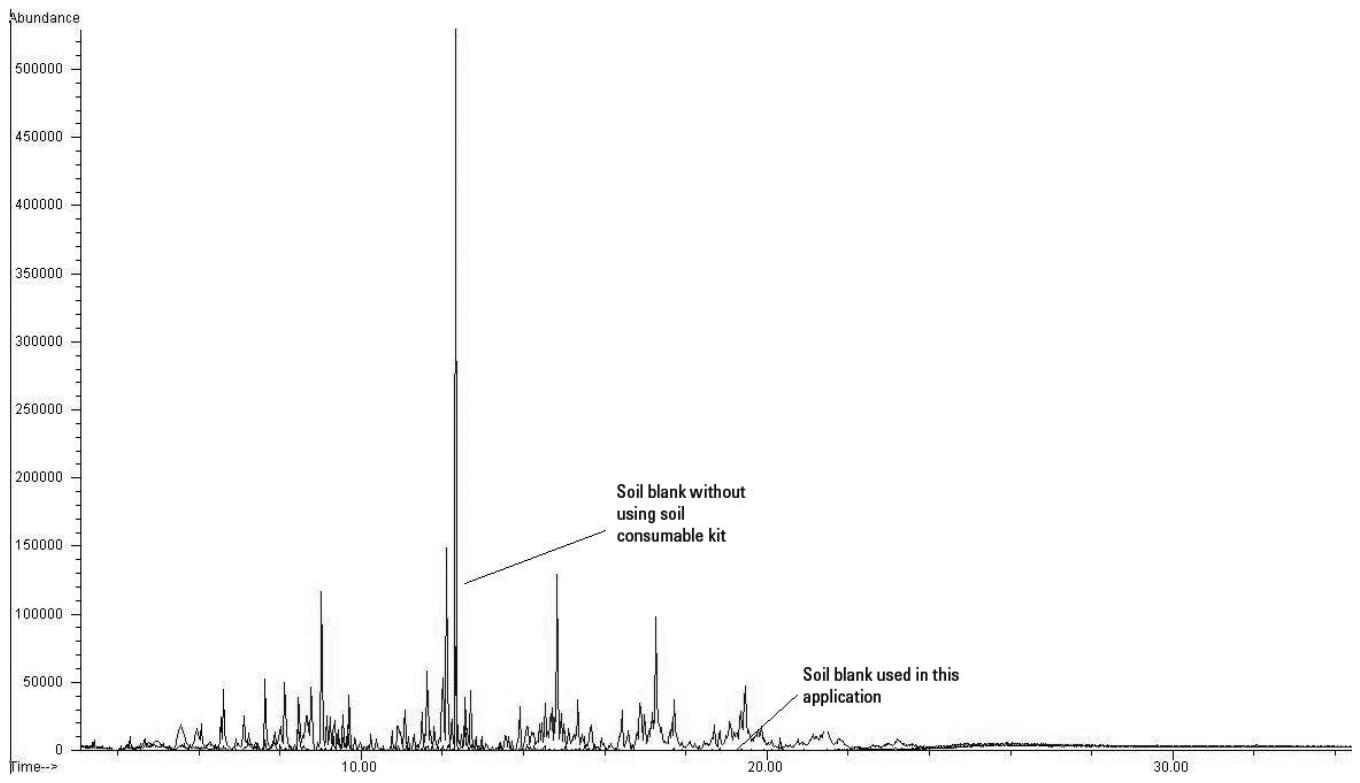


Figure 3. Overlay of the soil blanks with and without QuEChERS pretreatment.

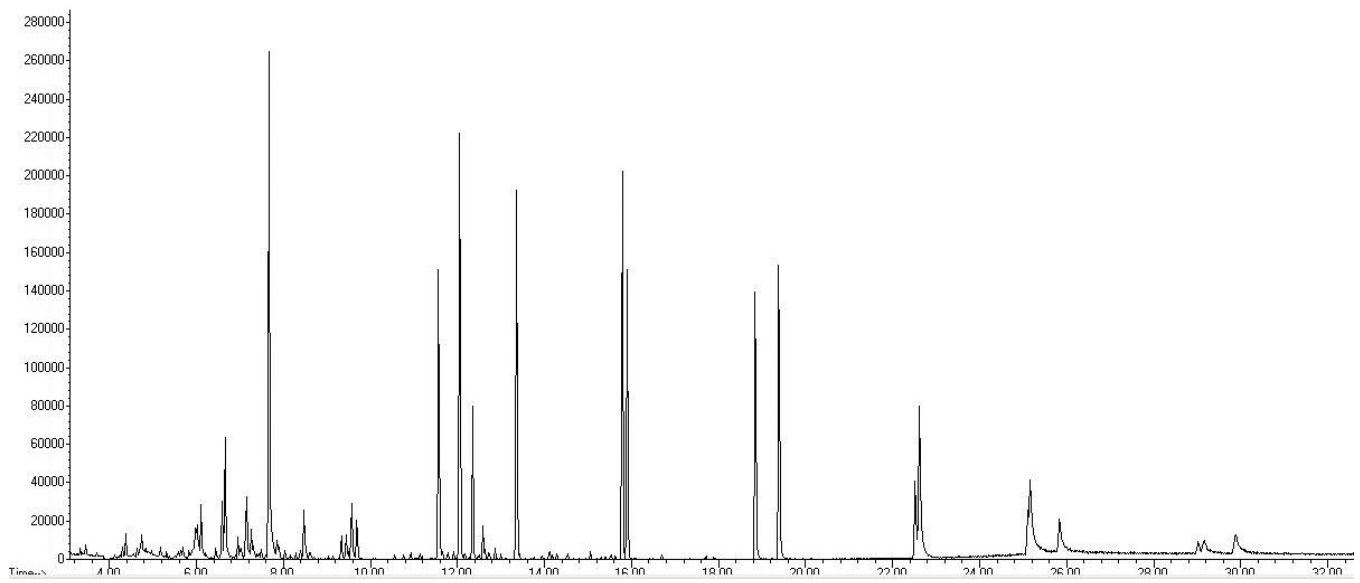


Figure 4. The PAHs standard solution at a 1:100 dilution in soil matrix.

The data is screened within 30 seconds using the RTL database. All of the compounds listed in the screening library are identified. The screening report is listed in Table 2 positively identifying the target compounds in soil matrix.

Table 2. Screening Report of PAHs in Soil Matrix

Compound	Status	ExpRT	Delta	M/Z	Resp.	Out of Range	XCR
1 Naphthalene	x	7.665	-0.033	128	2729035	1.00	
2 Acenaphthylene	x	11.566	-0.008	152	5195249	1.00	
3 Acenaphthene	x	12.050	-0.010	153	1494087	1.00	
4 Fluorene	x	13.345	-0.020	166	254632	1.00	
5 Phenanthrene	x	15.787	-9.925	167	167846	1.00	
6 Anthracene	x	15.898	-0.020	178	150569	1.00	
7 Fluoranthene	x	18.844	-0.010	202	301843	1.00	
8 Pyrene	x	19.384	-0.005	202	141960	1.00	
9 Benz[a]anthracene	x	22.519	-0.018	228	37499	0.97	
10 Chrysene	x	22.614	-0.015	228	82114	1.00	
11 Benzo[b]fluoranthene	x	25.164	-0.078	252	56641	0.00	
12 Benzo[k]fluoranthene	x	25.195	-0.109	252	56651	0.00	
13 Benzo[a]pyrene	x	25.835	-0.025	252	20127	0.99	
14 Indeno[1,3,2-cd]pyrene	x	29.023	-0.056	276	3397	0.88	
15 Dibenz[a,h]anthracene	?	29.161	-0.040	278	19292	276	0.15
16 Benzo[ghi]perylene	x	29.885	-0.035	276	58107	0.98	

The Agilent RTL Results Screener, available in the workstation (Figure 5) can be used to confirm the results. The target ions are extracted and the overlay is shown in Figure 5a. The relative abundances of target ions and qualifiers are measured and compared to the library data and are shown in Figure 5c. The target spectrum is shown in Figure 5b.

Deconvolution of the Chromatogram using MDS-DRS Software

The DRS method is established and configured from the PAH chromatogram [3]. Once configured, it can extract the target from complex interferences and can semi-quantitatively determine the content of the target in certain matrices with the existing quantitation database. It can deconvolute the targets in levels of 0.01 µg/mL in soil. Table 4 contains a report of the “buried” components in the matrix.

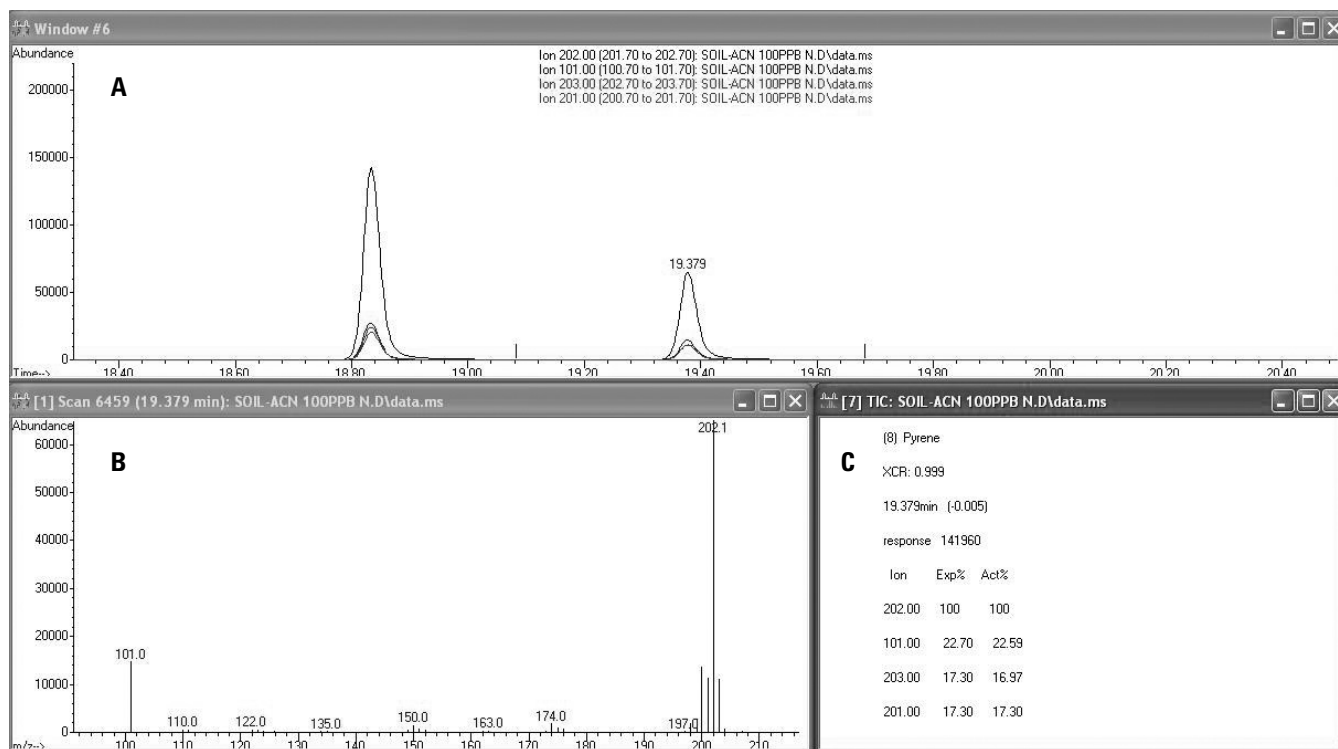


Figure 5. Example of screener results for pyrene.

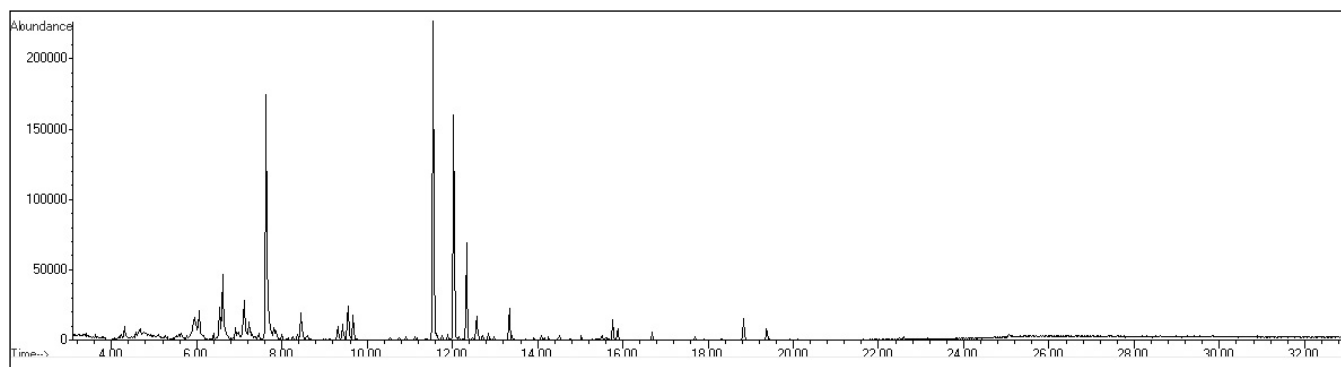


Figure 6. Dilution of the EPA610 mixture in soil matrix to 1000 times. The chromatogram shows that the later elutions were buried in the soil matrix.

Table 4. Partial DRS Report for Figure 6 Chromatogram.*

R.T.	CAS #	Compound name	Amount (ng)		AMDIS		NIST	
			ChemStation	AMDIS	Match	R.T. Diff sec.	Reverse Match	Hit Number
25.088	205992	Benzo[b]fluoranthene	0.03		99	-4.56	85	5
25.163	207089	Benzo[k]fluoranthene	0.02		99	-0.6	85	5
25.810	50328	Benzo[a]pyrene	0.01		98	-5.9	93	6
28.9685	193395	Indeno[1,2,3-cd]pyrene			87	-2.6	87	1
29.124	53703	Dibenz[a,h]anthracene	0.01		99	-2.2	85	5
29.8481	191242	Benzo[ghi]perylene	0.03		95	-2.1	87	2

*The quantitative results are only the estimated results based on a non-matrix response factor. There is no matrix calibration for the target PAHs.

Conclusion

This application note establishes a solution for analyzing PAHs in soil using the Agilent 5975T LTM GC/MSD. The solution contains a sample pretreatment procedure and a GC/MS instrument method. The SampliQ extraction QuEChERS kits prove to be a very suitable sample pretreatment technique for PAH analysis in soil. The benefits include time savings, simplicity, and reduced chemical reagent cost. Therefore this method is extremely complementary to the transportable Agilent 5975T LTM GC/MSD and its applications. Agilent's RTL function provides an excellent tool for quick peak identification especially in urgent cases where target compound identification is essential using a transportable GC/MS.

Reference

- 1 Frank David, Pat Sandra and Philip L. Wylie; "Improving the Analysis of Organotin Compounds using Retention Time Locked Methods and Retention Time Databases," Agilent Technologies publication 5988-9256EN.

- 2 Micheal J. Szelewski; Kenneth R. Weiner and Chin-Kai Meng; "Building and Editing RTL Screener/Quant Databases and Libraries," Agilent Technologies publication 5989-0916EN.
- 3 Philip L. Wylie, "A Rapid GCMS Solution for the Japanese Positive List Pesticide Method," Agilent Technologies publication 5989-9320EN.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc., 2011
Printed in the USA
February 11, 2011
5990-6324EN



Agilent Technologies