CHROM - APPS

YEAR: 2017 NUMBER: CHAP- 002

LANGUAGE: US / UK

SPME® - AUTOMATED QUANTITATIVE ANALYSIS OF WATER AND SOIL PROFILES BY MFX AND FAST GC/MS

OVERVIEW

The Italian Legislative Decree No 152/2006 implementing Directive 2001/42/EC sets out a series of analytical profiles for water and soil. Meeting this requirement can result in a considerable commitment in terms of human resources and equipment. In previous studies the use of solvents and/or clean-up steps are often reported to extract and eliminate most of the interfering compounds. This commonly results in a large number of manual operations, uncertainty of the determination, higher overall cost of the method, and possible analyte loss. Accordingly, procedures were developed

Fig. 1. New SPME-FFA fibers, patented and produced by Chromline Srl.

where the properties of HS/DI-SPME technique as well as the automation of the preparation procedure by new robotic system called MultiFibre Exchange System (MFX), allowing automated exchange of the fibres, providing a convenient and more efficient use of a Fast-GC-MS/EI instrument with a number of advantages including reduced analyst time and greater reproducibility.

AUTOMATION

Since the determination of the four profiles requires different fibres, the object of this paper was focused on the automation of the SPME extraction procedure and on the Fast GC/MS performance. Commonly a change of a fibre on an autosampler requires manual interaction by the operator and causes a delay in sample analysis. The three polydimethylsiloxane PDMS (PDMS) fibres (7, 30, and 100 µm) selected for this study were used simultaneously on the 6-position MFX System installed on a 3-axis system (Fig. 2).

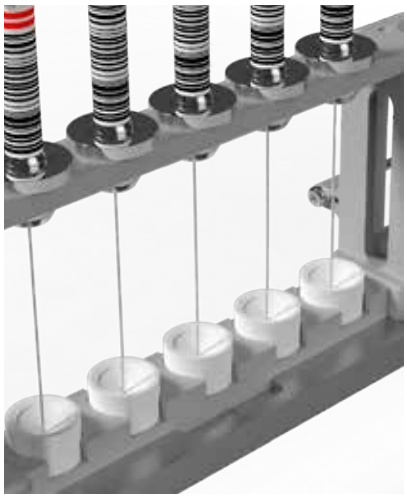


Fig. 3. MFX sealing system.

MFX System is also available in other versions that can also housing 3, 25 and 45 fibers.
The used fibres were all SPME-Fast Fit Assemblies (SPME-F-FA), a new fibre configuration (Supelco®, Sigma-Aldrich, Milan, Italy).
The FFA configuration allows the use of multiple SPME fibres on the MFX system in fully automated processes, by means of automatically exchanging the used fibre on the system. The FFAs are more robust and easier to use, without the need of screwing them into a fibre holder, and they are barcoded for reliable identification. In this study, the 3 fibres used were transported between the 3 of 6-position fibre tray of the MFX and the vials, containing water or soil, and the injector by the magnetic MFX holder.
At the end of the analysis, the desorbed fibre is moved back to the tray and the cycle is repeated with the next phase. Moreover, the autosampler parameters also allowed a complete analysis cycle incorporating also the conditioning step by first conditioning each fibre and then placing them back in the tray where they are sealed off by a spring-loaded Teflon® cone (Fig. 3).

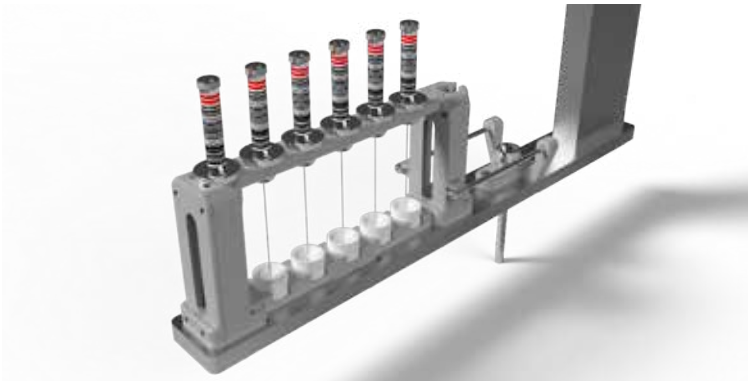
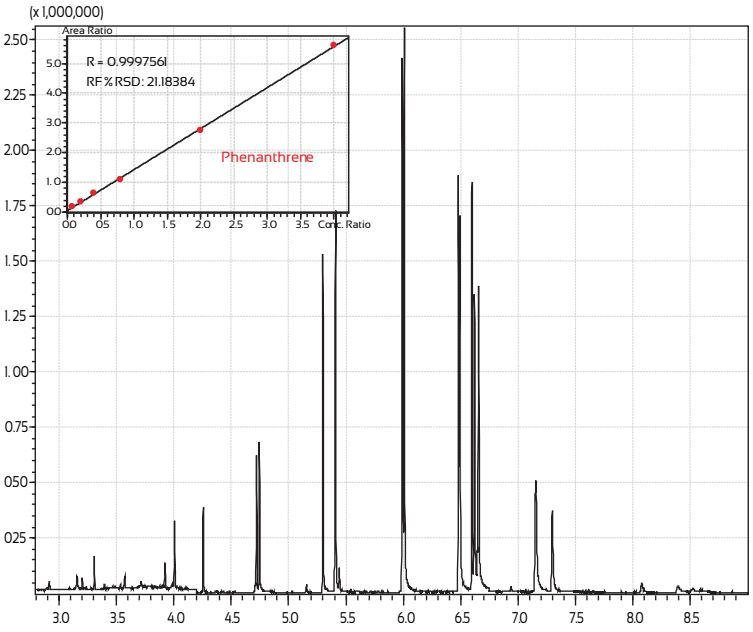


Fig. 2. MFX-6 system.



Sample: 10 mL water
SPME Fibre: 7 µm PDMS, SPME/Direct Immersion 20 min @ 40 °C
Desorption: 280 °C, splitless, 2.50 min
CarrierGas: Helium 60.0 cm/sec
Oven: 40 °C, 1 min hold, 50 °C/min to 320 °C, 3 min hold
Detector: MS, SIM, Ion Source Temp: 240 °C

	Analyte Listing	RT			RT			RT
1)	Naphthalene	3.156	8)	Anthracene	4.745	16)	B(k)Fluoranthene	6.492
2)	Acenaphthylene	3.922	9)	Fluoranthene	5.300	17)	B(e)Pyrene	6.599
3)	Acenaphthene D10	3.991	10)	Pyrene D10	5.401	18)	B(a)Pyrene	6.620
4)	Acenaphthene	4.007	11)	Pyrene	5.410	19)	Perylene D12	6.645
5)	Fluorene	4.257	12)	B(a)anthracene	5.990	20)	Perylene	6.656
6)	Phenanthrene D10	4.710	13)	Crysene D12	5.996	21)	I(123cd)Pyrene	7.150
7)	Phenanthrene	4.721	14)	Crysene	6.008	22)	DB(ah)anthracene	7.157
			15)	B(b)Fluoranthene	6.481	23)	B(ghi)Perylene	7.298

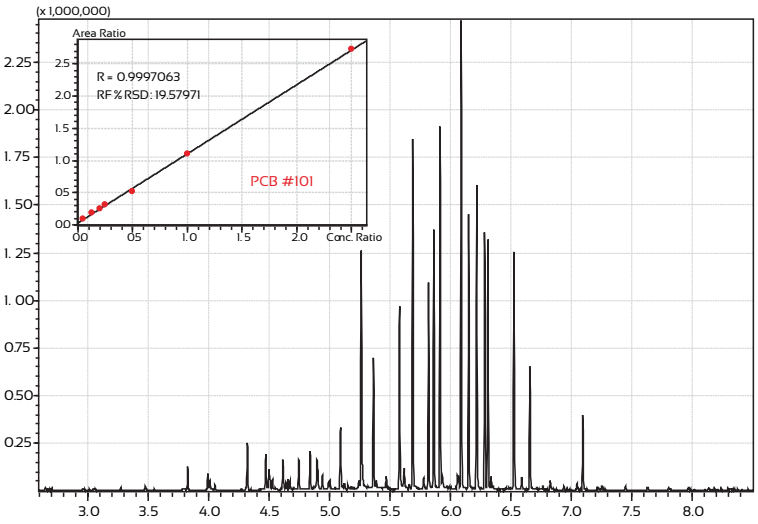
Fig. 4. Poly aromatic hydrocarbons (PAHs) at 5 ng/L.

FAST GC/MS CONDITIONS

The Fast GC-MS conditions are outlined in Figures 3 to 6. The Shimadzu® GC/MS-EI 2010 (Shimadzu Italia, Milan, Italy) was equipped with SLB™-5ms column (10 m, 0.10 mm internal diameter, 0.1 µm film thickness, Supelco/Sigma-Aldrich, Milan).

CHROMLINE SRL

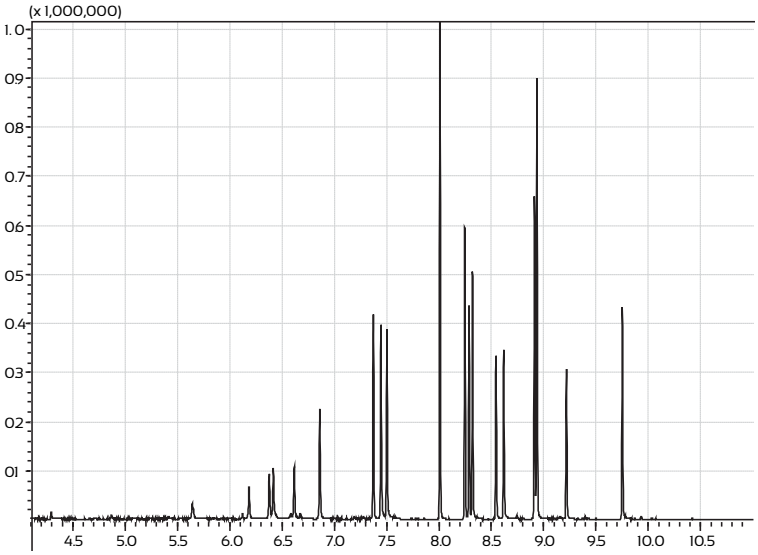
Via A. De Gasperi 41 - 59100 - Prato (Italy)
+39 05741746197 - +39 05741741042
info@chromlinesrl.com - www.chromlinesrl.com

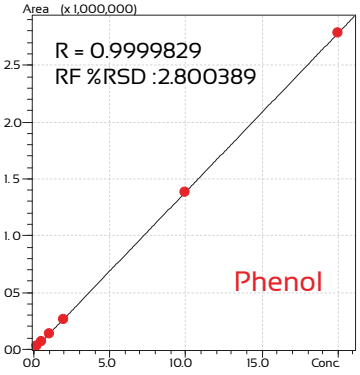


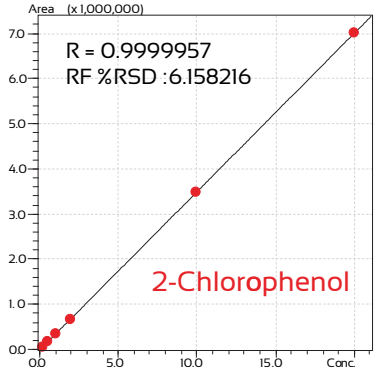
Sample: 1g soil in 10 mL water
SPME: 30 µm PDMS, SPME/HS 5 min @ 90 °C
Desorption: 275 °C, Splitless, 2.50 min Carrier Gas: Helium 49.5 cm/sec
Oven: 60 °C, 1 min hold, 40 °C/min to 340 °C, 0.50 min hold
Detector: MS, SIM, Scan Width: 0.10 amu, Ion Source Temp: 240 °C

	Analyte Listing	RT						
1)	#1	4.009	9)	#66	5.579	18)	#138 C13	6.216
2)	#5	4.615	10)	#101 C13	5.688	19)	#138	6.217
3)	#18	4.839	11)	#101	5.689	20)	#187	6.284
4)	#31	5.090	12)	#87	5.819	21)	#183	6.310
5)	#28 C13	5.093	13)	#110	5.862	22)	#180 C13	6.524
6)	#52 C13	5.262	14)	#151	5.914	23)	#180	6.525
7)	#52	5.263	15)	#153 C13	6.088	24)	#170	6.656
8)	#44	5.363	16)	#153	6.089	25)	#206	7.095
			17)	#141	6.151			

Fig. 5. PCBs at 2.5 ng/L.



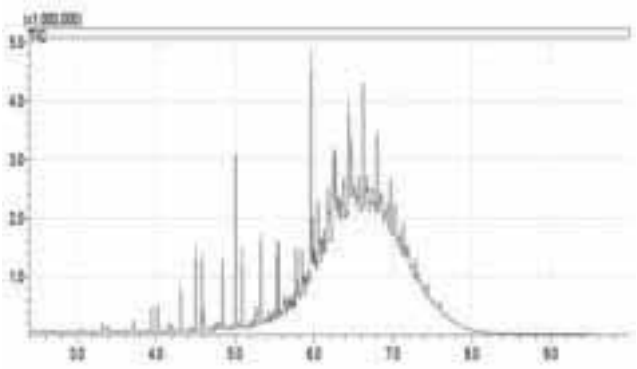




Sample: 10 mL water
SPME: 100 µm PDMS, SPME/HS 15 min @ 60 °C, after in situ acetylation by acetic anhydride(1) with 50 µL acetic anhydride + 0.2 g KHCO3
Desorption: 260 °C, splitless, 2.0 min Carrier Gas: Helium 45.0 cm/sec
Oven: 40 °C, 3 min hold, 25 °C/min to 240 °C
Detector: MS, SIM, Scan Width: 0.10 amu, Ion Source Temp: 240 °C

	Analyte Listing	RT			
1)	Phenol	5.648	10)	2,3,5-Trichlorophenol	8.009
2)	2-Methyl phenol	6.184	11)	2,4,6-Trichlorophenol	8.247
3)	3-Methyl phenol	6.378	12)	2,4,5-Trichlorophenol	8.288
4)	4-Methyl phenol	6.417	13)	2,3,4-Trichlorophenol	8.320
5)	2-Chloro phenol	6.617	14)	2,3,6-Trichlorophenol	8.545
6)	2,4-Dimethylphenol	6.861	15)	3,4,5-Trichlorophenol	8.619
7)	2,4-Dichlorophenol	7.373	16)	2,3,5,6-Tetrachlorophenol	8.913
8)	4-Chloro-3-methylphenol	7.446	17)	2,3,4,5-Tetrachlorophenol	8.936
9)	2,6-Dichlorophenol	7.502	18)	2,3,4,6-Tetrachlorophenol	9.218
			19)	Pentachlorophenol	9.753

Fig. 6. Phenols at 500 ng/L



Sample: 10 ml water + 300 mg (NH4)2SO4
SPME: 7 µm PDMS, SPME/HS 15 min @ 120 °C (incubation 5 min)
Desorption: 320 °C, splitless, 2.00 min Carrier Gas: Helium 55.0 cm/sec
Oven: - 60 °C, 1 min hold, 40 °C/min to 340.0 °C, 2 min hold
Detector: MS, ACQ Mode SIM: Ch1-m/z :55.00, Ch2-m/z :57.00, Ch3-m/z :71.00, Ch4-m/z :83.00, Ch5-m/z :85.00, Ch6-m/z :66.00. Ion Source Temp: 240 °C

Fig. 7. BAM K010 50 µg/L

ANALYTICAL METHODS

Samples: 10 mL water or 1 g soil in 10 mL water, 20 ml vial

PAH: 7 µm PDMS, SPME/Direct Immersion (DI) 20 min @ 40 °C;

PCBs: 30 µm PDMS, SPME/Head Space (HS) 5 min. @ 90 °C;

Phenols: 100 µm PDMS, acylation by 50 µL acetic anhydride, 0.2 g KHCO3, SPME/HS 15 min @ 60°C (1)

BAM K010: 7 µm PDMS, [300mg (NH4)2SO4], SPME/HS: incubation 5 min @ 120 °C, sampling: 15 min (quail/quantitative).

RESULTS

The resulting calibration curves were linear, in the investigated range (Figure 3–6) for all compound profiles, with correlation coefficients >0.998. The resulting RSDs were ≤10%.

CONCLUSION

The automation of the preparation procedure with the MFX system on a XYZ type autosampler, allows the automated and unattended exchange of SPME-fibres. This enables the a more efficient use of a Fast-GC/MS instrument providing a number of benefits including reduced analyst time for both routine analysis and method development and greater reproducibility.

REFERENCES

1. Automated High-Throughput Quantitative Analysis of Water and Soil Profiles by MultiFibre Exchange-SPME Coupled to Fast GC/MS. Stefano Dugheri, Alice Bonacchi, Giulio Arcangeli, Vincenzo Cupelli (Laboratorio di Igiene e Tossicologia Industriale, Largo Palagi 1, Careggi Hospital-University of Florence, 50100 Florence) Rino Calori, Manuela Di Giovanni, Maria Ferrari, Barbara Romagnoli, Maurizio Falchieri, Cecilia Bergamini (Laboratorio Integrato Unità strumentale ARPA Emilia-Romagna-Nodo di Bologna) Filippo Degli Esposti, Nicola Perchiazzi, Gionni Capacci (Chromline Srl, Via Anita Garibaldi 40, 59100 Prato, Italy) Edoardo Salvadori, Alida Falai, Maurizio Cappelli, Daniela. Santianni, Daniela Burrini (Publiacqua S.p.A. Via Villamagna 90/c, 50126 Firenze).

SRA INSTRUMENTS SpA
Via alla Castellana, 3
20063 Cernusco S/N (MI) I Italy
Tel. +39 02 9214 3258
Fax +39 02 9247 0901
info@srainstruments.com

SRA INSTRUMENTS SAS
210 rue des Sources
69280 Marcy l'Etoile I France
Tel. +33 (0)4 78 44 29 47
Fax +33 (0)4 78 44 29 62
info@sra-instruments.com

srainstruments.com