Environmental

Automated dispersive liquid-liquid micro extraction (DLLME) for GC-MS/MS analysis of semi-volatile compounds in water

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Keywords

Water analysis, pesticides, polyaromatic hydrocarbons (PAHs), dispersive liquid-liquid micro extraction (DLLME), automation, TriPlus RSH SMART autosampler, TRACE 1610 GC, TSQ 9610 GC-MS/MS, AEI ion source

Goal

To demonstrate the analytical performance of the automated dispersive liquid-liquid micro extraction (DLLME) sampling technique on-line with a highly sensitive GC-MS/MS analysis to meet the most demanding regulatory requirements for the determination of pesticides and polyaromatic hydrocarbons (PAHs) in water samples. This approach reduces manual labor time through automation and ensures high data quality.

Introduction

Environmental contaminants remain a constant cause of concern for the public and there is a constant need for laboratories to analyze samples in a fast and cost-effective way. To accomplish that, laboratories look for options that minimize sample preparation time and reduce solvent usage and disposal costs without compromising the quality of the analytical results.

The European Union (EU) Water Framework Directive[1] was introduced in August 2013, amending EU Directives 2000/60/EC and 2008/105/EC and laying down a strategy against the pollution of water to be applied to all EU member states. This strategy involves the identification of priority substances and the monitoring of different classes of contaminants, such as several pesticide compounds. Practically, however, every member state is responsible for implementing applicable legislation based on the

Water Framework Directive as a minimum requirement. In the United Kingdom (UK), the Chemical Investigation Program 2 (CIP2) UK regulations[2] investigate the occurrence, sources, and removal of trace substances in wastewater treatment facility effluents. This regulation helps to establish priorities for premeditative action to ensure surface waters meet new environmental quality standards (EQS). Italian legislation is particularly stringent with respect to the required LOQ and maximum deviation for drinking water (DL 18/23), surface, ground, and wastewater (DL 152/06) and poses challenges to the water laboratories in terms of monitoring the various compounds as very low detection limits are required. Thus, being able to reach these levels would require an investment in advanced laboratory equipment as well as a different approach to sampling.

Traditional manual extraction and clean up procedures, such as solvent extraction and solid phase extraction (SPE), require large amounts of water sample and extraction solvents, as well as extensive labor time. The development over the last decade of liquid phase microextraction techniques allows the amount of sample and solvent volumes to be scaled down, therefore reducing costs and offering a more environmentally friendly approach.

DLLME is a sample preparation technique widely used in analytical chemistry for the extraction and preconcentration of trace analytes from liquid samples. This method is particularly effective for the analysis of organic compounds in various matrices, including water, beverages, biological fluids, and environmental samples. The DLLME technique utilizes a reduced amount of extraction solvent (in the order of few hundreds of microliters) dispersed as fine droplets in a limited amount of sample (i.e., 5–10 mL). A polar dispersive co-solvent is used to generate the emulsion. This dispersion increases the surface area of the extracting solvent, facilitating the transfer of analytes from the aqueous phase to the organic phase.

DLLME offers several advantages, including high enrichment factors, low solvent consumption, and rapid extraction times. It is particularly well-suited for the extraction of hydrophobic and semi-polar compounds, while the method may have limitations in terms of extraction efficiency for highly polar analytes. Additionally, the technique can be easily automated using a robotic autosampler.

This application note describes an automated workflow using DLLME followed by on-line large volume injection (LVI) and GC-MS/MS analysis for the determination of target non-polar pesticides and polyaromatic hydrocarbons (PAHs) in drinking water samples. The workflow ensures optimal sensitivity at sub-ppt levels[3] and therefore can meet the Italian directive guidelines for method validation in terms of limit of quantitation (LOQ) and precision. Full automation of the sample preparation procedure offers not only significant labor-time savings for the analyst but removes the variability of manual operation to deliver higher quality data.

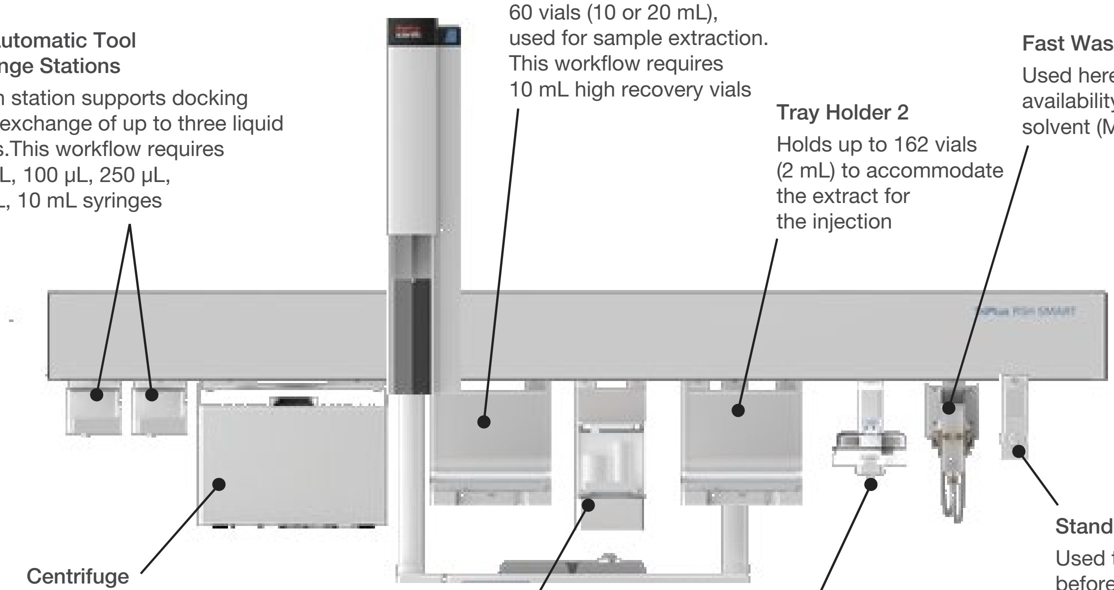
Experimental

A dedicated configuration of the Thermo Scientific™ TriPlus™ RSH SMART robotic autosampler (Figure 1) was used to automatically execute all the steps of the DLLME sample preparation. The workflow script was programmed by SampleQ, Breda, NL.[4] The automated workflow allows sample and solvent volumes to be scaled down, therefore significantly reducing operational costs.

The steps to perform the DLLME are summarized in Figure 2: a small amount of dispersive solvent (methanol) is added to 9.5 mL high-recovery vials (P/N 6PCV10-V1; caps: P/N 6PBCC20-ST3) previously filled with 5 mL of water sample. The dispersive solvent will promote the emulsion with water for a more efficient partitioning of the analytes. The extraction solvent (dichloromethane (DCM), 0.4 mL) is then added to extract the analytes of interest.

Solvent addition is followed by thorough mixing using the vortex mixer module for 60 s, and a subsequent centrifugation for 90 s.

The centrifugation step is necessary to break the emulsion and separate the low amount of the extraction solvent from the aqueous phase. After centrifugation, the DCM layer (deposited on the bottom of the vial) is recovered and transferred to 0.3 mL microvials (P/N 6PSV9-03FIVP; caps P/N 6PSC9ST101), ready to be injected. The use of the 9.5 mL high recovery vials is critical to allow the recollection of the DCM extract after the centrifugation step.



2x Automatic Tool Change Stations
Each station supports docking and exchange of up to three liquid tools.This workflow requires 50 µL, 100 µL, 250 µL, 1 mL, 10 mL syringes

Tray Holder 1
Used for sample storage. This tray holder holds up to 60 vials (10 or 20 mL), used for sample extraction. This workflow requires 10 mL high recovery vials

Tray Holder 2
Holds up to 162 vials (2 mL) to accommodate the extract for the injection

Fast Wash Module
Used here to provide longer availability of dispersive solvent (MeOH)

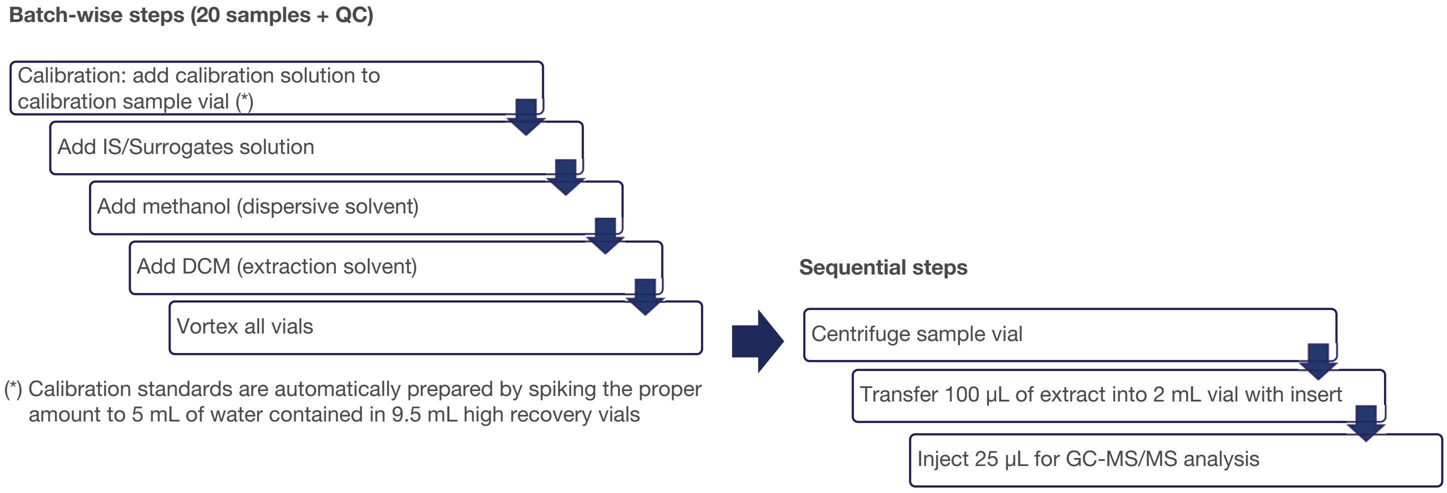
Centrifuge
Supports centrifugation of 2, 10 or 20 mL vials. The centrifugation step facilitates phase separation after solvent extraction

Vortex Mixer
Used to add a stirring step during the extraction step

Solvent Station
Used for solvent/calibration/ IS solution storage

Standard Wash Station
Used to wash the syringes before/after IS addition and prior to injection with different solvents for one or more of washing cycles

Figure 1. TriPlus RSH SMART autosampler configuration for automated DLLME



Batch-wise steps (20 samples + QC)

- Calibration: add calibration solution to calibration sample vial (*)
- Add IS/Surrogates solution
- Add methanol (dispersive solvent)
- Add DCM (extraction solvent)
- Vortex all vials

(*) Calibration standards are automatically prepared by spiking the proper amount to 5 mL of water contained in 9.5 mL high recovery vials

Sequential steps

- Centrifuge sample vial
- Transfer 100 µL of extract into 2 mL vial with insert
- Inject 25 µL for GC-MS/MS analysis

Figure 2. Automated DLLME workflow with on-line LVI and GC-MS/MS analysis

The small volume of solvent used for extraction allows an approximate 15-fold higher enrichment compared to standard liquid-liquid extraction (LLE). At the same time, the required sample volume is reduced from 1 L (manual LLE protocol) down to about 5 mL. A large volume injection (LVI) is then performed by injecting 25 µL of sample in solvent split mode into a Themo Scientific™ iConnect™ PTV injector installed on a Thermo Scientific™ TRACE™ 1610 gas chromatograph. Moreover, the coupling with the highly sensitive Thermo Scientific™ TSQ™ 9610 triple quadrupole mass spectrometer, equipped with the Thermo Scientific™ Advanced Electron Ionization (AEI) source, completes the analytical system allowing for detection limits down to sub-ppt levels. A dedicated MS Smart Tuning is available to be executed before each sequence in compliance with United States Environmental Protection Agency (EPA) Method 8270. The instrumental parameters are detailed in Table 1, and the selected reaction monitoring (SRM) transitions for the investigated compounds are reported in Appendix Table A1.

Calibration standards

To assess instrument performance, the following standard solutions were prepared:

- PAH stock solution: 500 µg/mL in acetonitrile (≥99.8%, Fisher Scientific P/N 15664670) / acetone (>99.8%, for pesticide residue analysis, Fisher Scientific P/N 15624190) / toluene (>99.8%, Fisher Scientific P/N 10164240)
- Pesticide stock solution: 200 µg/mL in acetone
- Pesticide OCP: 200 µg/mL in acetone
- Chlordane: 200 µg/mL in acetone
- ISTD stock solution: 4,000 mg/L (diluted to 10,000 µg/L)
- Surrogate stock solution: 4,000 mg/L (diluted to 10,000 µg/L)

The stock solutions were furtherly diluted in methanol (≥99.8%, GC-MS grade, Fisher Scientific P/N 15623710) to obtain the working solutions used to prepare the calibration curve:

- Analyte working solution 1 (high): 50 µg/L
- Analyte working solution 2 (medium): 5 µg/L
- Analyte working solution 3 (low): 0.5 µg/L
- ISTD and surrogate working solutions: 50 µg/L

Table 1. GC-MS/MS instrumental parameters

iC-PTV parameters	
Injection temperature (°C)	40
Liner	Deactivated sintered liner (P/N 45352060)
Injection mode	LVI Solvent Split
Injection volume (µL)	25
Injection time (min)	0.6
Injection split flow (mL/min)	20
Transfer rate (°C/s)	8.0
Transfer temperature (°C)	310
Transfer time (min)	2.00
Splitless time (min)	2.00
Cleaning rate (°C/s)	14.5
Cleaning temperature (°C)	320
Cleaning time (time)	10.00
Cleaning split flow (mL/min)	50
Transfer delay time (min)	1.00
Post cycle temperature	Maintain
Split flow (mL/min)	10
Septum purge flow (mL/min)	5, constant
Carrier gas, flow (mL/min)	He, 0.8

TRACE 1610 GC parameters	
Oven temperature program	
Oven equilibration time (min)	0.1
Temperature (°C)	40
Hold time (min)	3.0
Rate (ºC/min)	20
Temperature 2 (°C)	320
Rate (ºC/min)	5
GC run time (min)	22.00
Column	
Thermo Scientific™ TraceGOLD™ TG-5SilMS	20 m, 0.18 mm, 0.18 µm (P/N 26096-5780)

TSQ 9610 mass spectrometer parameters	
Transfer line temperature (°C)	320
Ion source type and temperature (°C)	NeverVent™ AEI, 290
Ionization type	EI
Emission current (µA)	10
Aquisition mode	Timed-SRM
Tuning parameters	AEI SmartTune
Detector gain	7
Collision gas and pressure (psi)	Argon at 60

Nine calibration levels, ranging from 0 to 1 µg /L, were automatically prepared in 9.5 mL high recovery vials pre-filled with 5 mL of ultrapure water by the TriPlus RSH autosampler according to the scheme reported in Table 2. The ISTD (25 µL) and surrogate solutions (25 µL) were automatically added to each calibration vial prior to start the DLLME process.

Table 2. Dilution scheme of the calibration solutions

Calibration level	Concentration (µg/L)	Analyte working solution 1 (µL)	Analyte working solution 2 (µL)	Analyte working solution 3 (µL)	Methanol (µL)	ISTD/surrogate working solution
0	0	-	-	-	100	25
1	0.0005	-	-	5	95	25
2	0.002	-	-	20	80	25
3	0.01	-	10	-	90	25
4	0.05	-	50	-	50	25
5	0.1	-	100	-	-	25
6	0.25	25	-	-	75	25
7	0.50	50	-	-	50	25
8	1.0	100	-	-	-	25

Sample preparation

Samples of water intended for human consumption were prepared by pipetting 5 mL of water into 9.5 mL high recovery vials and positioning them on the autosampler tray. The addition of ISTD/SURR (25 µL) and the DLLME procedure were automatically executed by the autosampler.

Data acquisition, processing, and reporting

The automated workflow and the entire analytical system are fully controlled by the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3, used for data acquisition, data processing, reporting, and storage in compliance with the United States Food and Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11). Additionally, the optional interfacing with LIMS software enhances overall laboratory efficiency and data management.

The system takes about 2 h to prepare and extract a batch of 20 samples plus the QC samples, as required by the EPA Method 8270 used as reference method for internal accreditation, followed by 22 min of GC run and 5 min of GC cooling per sample. The sequential operations after the preparation in batch, including centrifugation and transfer of the extract into the empty vial, are executed during the GC run of the previous sample, optimizing the overall cycle time.

Results and discussion

The implementation of the automated DLLME workflow with on-line GC-MS/MS analysis allowed for method consolidation with the analysis of 70 analytes including PAHs and pesticides in one single run. Compared to a previous manual approach with different methods for pesticides and PAHs, the current workflow offers a significant reduction of labor time and a significant reduction of solvent consumption, thanks to the miniaturization of the volumes. A typical chromatogram after DLLME of a calibration standard in water at 0.05 µg/L is shown in Figure 3.

Linearity

The linear response was evaluated in the concentration range from 0 to 1 µg/L by using the internal standard method. The majority of the analytes showed a linear trend over the entire calibration range with a coefficient of correlation (R^2) > 0.999. An example of the calibration curve for pirimicarb obtained through automated dilution is reported in Figure 4. Please refer to Appendix Table A2 for the calibration curve details of the target analytes.

Limit of quantitation (LOQ)

The purpose of this method was the simultaneous analysis of 70 analytes including pesticides and PAHs, with quantitation limits between 0.0005 µg/L and 0.02 µg/L.

As per laboratory internal procedure, the lowest point of the calibration curve was selected as the limit of quantitation even if the results obtained during the validation phase suggest that lower quantitation limits can potentially be achieved for many of these compounds that show very good peak-to-peak signal-to-noise (S/N) ratios for both quantifier and qualifier ions. Examples are shown in Figure 5.

Compound name	Peak number	Compound name	Peak number	Compound name	Peak number	Compound name	Peak number
1,4-Dichlorobenzene-d4	1	Propazine	19	Metolachloor	37	Endrin	54
Naphthalene-d8	2	Atrazine-desethyl	20	Chloorpyriphos-ethyl	38	*b*-Endosulfan	55
Naphthalene	3	*g*-Hch	21	Parathion-ethyl	39	*p,p*-Ddd	56
2-Fluorobiphenyl	4	Terbutylazine	22	Aldrin	40	*o,p*-Ddt	57
Acenaphthylene	5	Diazinon	23	Isodrin	41	*p,p*-Ddt	58
Acenaphthene-d10	6	Phenanthrene-d10	24	*t*-Heptachloorepoxide	42	Benz(a)anthracene	59
Acenaphthene	7	Phenanthrene	25	Fluoranthene	43	Chrysene-D12	60
Molinat	8	Anthracene	26	*c*-Chlordane	44	Chrysene	61
Fluorene	9	*d*-Hch	27	o,p-Dde	45	Azinphos-methyl	62
Propachloor	10	Pirimicarb	28	Pyrene	46	Azinphos-ethyl	63
2,4,6-Tribromophenol	11	Parathion-methyl	29	*t*-Chlordane	47	Benzo(*b*)fluoranthene	64
Trifluralin	12	Alachlor	30	*a*-Endosulfan	48	Benzo(*k*)fluoranthene	65
Desethylterbutylazine	13	Ametryn	31	Oxadiazon	49	Benzo(*a*)pyrene	66
a-Hch	14	Prometryn	32	*p,p*-Dde	50	Perylene-d12	67
Hcb	15	Heptachloor	33	*p*-Terphenyl-d14	51	Indeno(*1,2,3-cd*)pyrene	68
Simazine	16	Terbutryn	34	*o,p*-Ddd	52	Dibenz(*a,h*)anthracene	69
Atrazine	17	Linuron	35	Dieldrin	53	Benzo(*ghi*)perylene	70
b-Hch	18	Malathion	36				

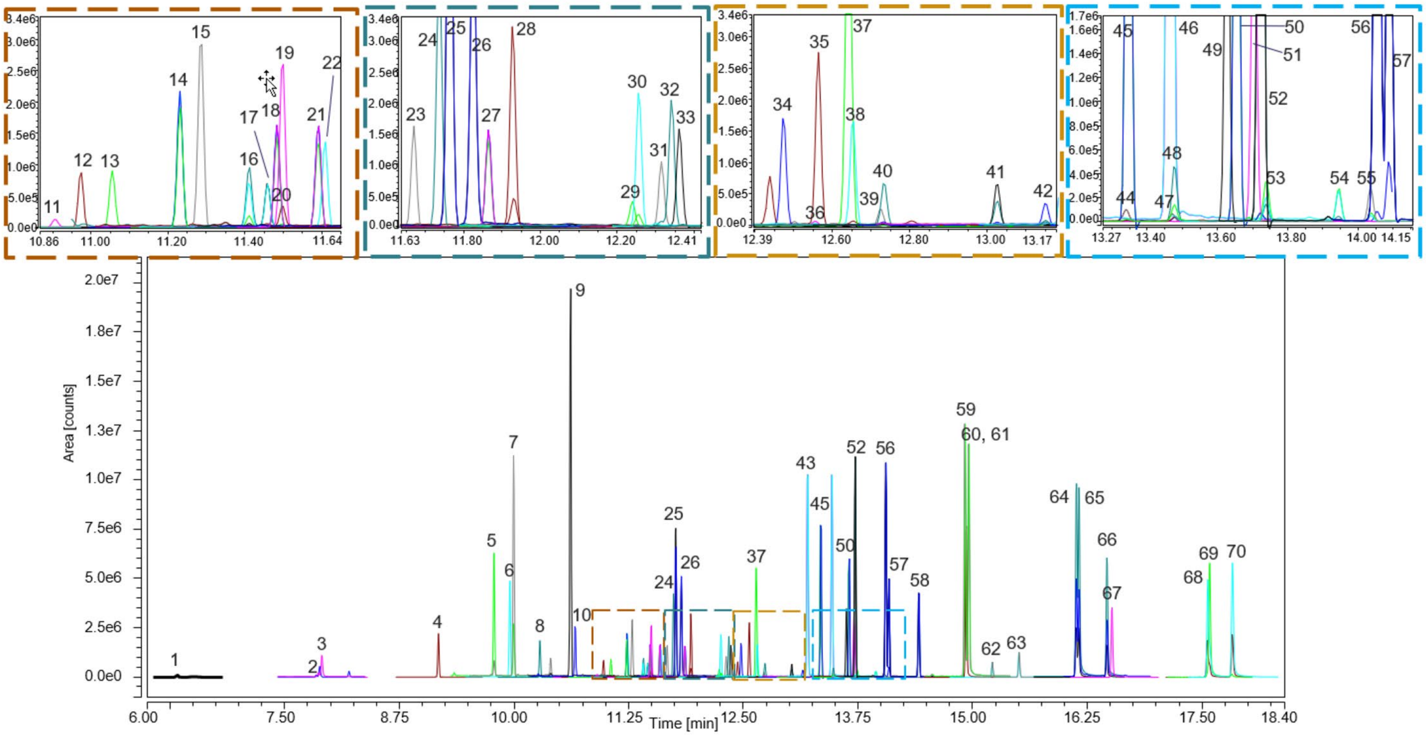


Figure 3. Typical chromatogram of a DLLME of a calibration standard in water at 0.05 µg/L

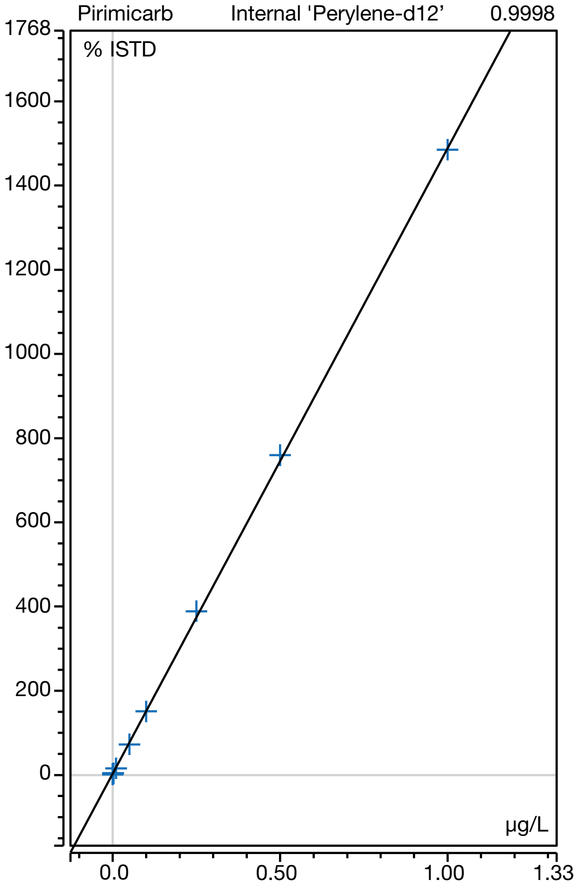


Figure 4. Calibration curve for pirimicarb in the concentration range from 0 to 1 µg/L, over nine concentration levels

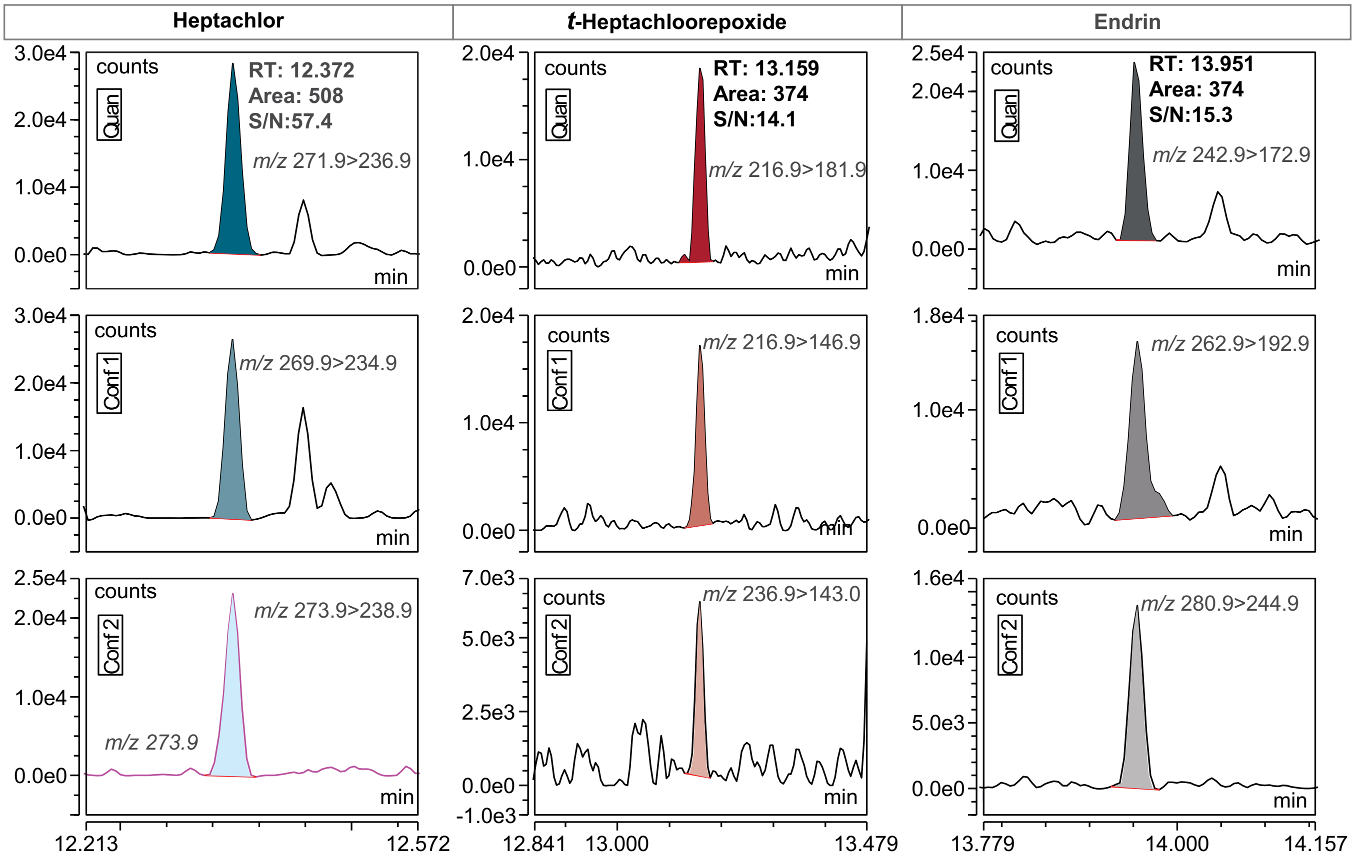


Figure 5. Examples of quantitation and qualification ions for some selected analytes at 0.0005 µg/L in water

The SRM acquisition mode offered high sensitivity to expand the list of the target analytes to other compounds such as deltamethrin and BDE138 (Figure 6).

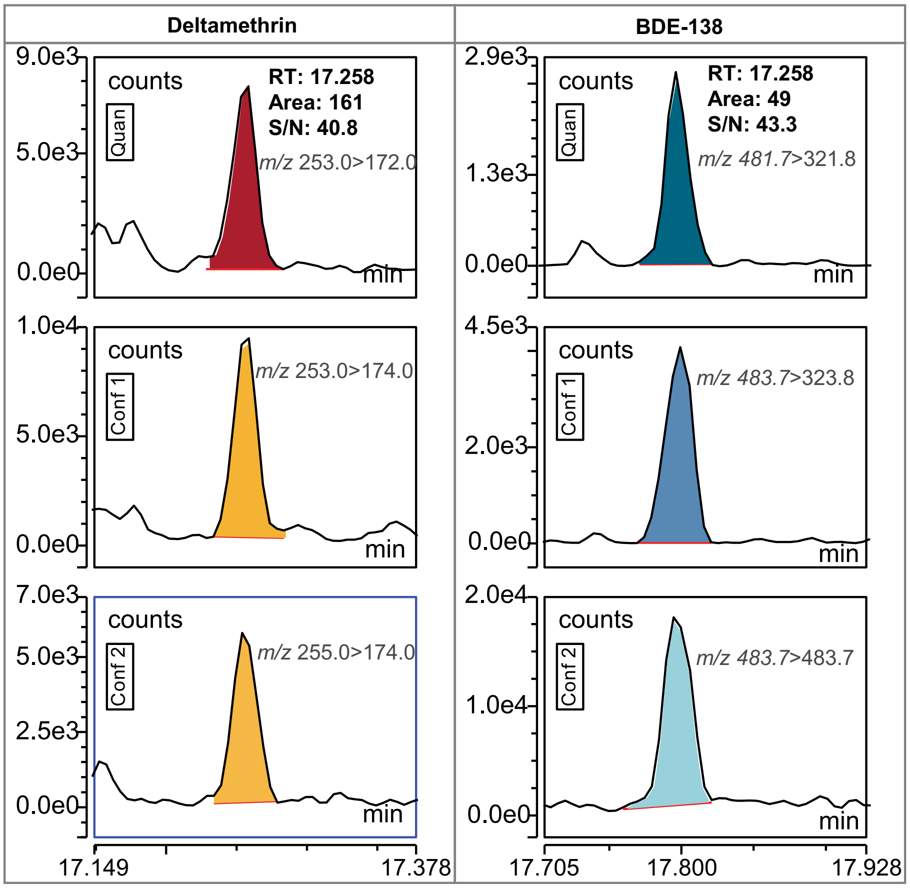


Figure 6. Examples of compounds (deltamethrin, BDE-138) that are not currently included in the list of the target analytes but that could be added to the analytical run for future proof analysis

The high sensitivity provided by the system and the very good peak-to-peak S/N allowed validation of a single analytical method that can be applied for the analysis of both clean water and wastewater samples because it is possible to make appropriate dilutions and still get the required limit of detection. The advantage is to use the same calibration curves for all the different aqueous matrices, simply adopting a suitable initial dilution for the most complex matrices. So, even for dirty water samples, the values of the quantitation limits, although corrected for the dilution factors, are compliant with the most stringent regulatory requirements.

Repeatability and minimum detectable level (MDL)

The repeatability test was executed by automatically extracting and injecting n=10 calibration standards at 0.01 µg/L. The relative standard deviation (%RSD) of the component calculated amount resulted <10% as reported in Figure 7, therefore meeting the method validation requirement typically laying between 10% and 25%.

The MDL calculated for some PAHs using the repeatability of the entire workflow at a value of 0.001 µg/L is reported as an example in Table 3, showing a limit of detection at sub-ppt levels.

Savings through automation

The automated DLLME approach was compared with the manual protocol previously used in the laboratory for the analysis of PAHs and pesticides in which manual SPE was followed by off-line GC-MS analysis and the application of different analytical methods for the two classes of compounds. In addition to the opportunity to consolidate the analysis of the target contaminants in one single method, the automated approach allowed for significant reduction in solvent consumption and sample volume with positive impact on the logistic costs of transportation and storage, improving the overall quality of the data streamlining the data processing, as summarized in Table 4.

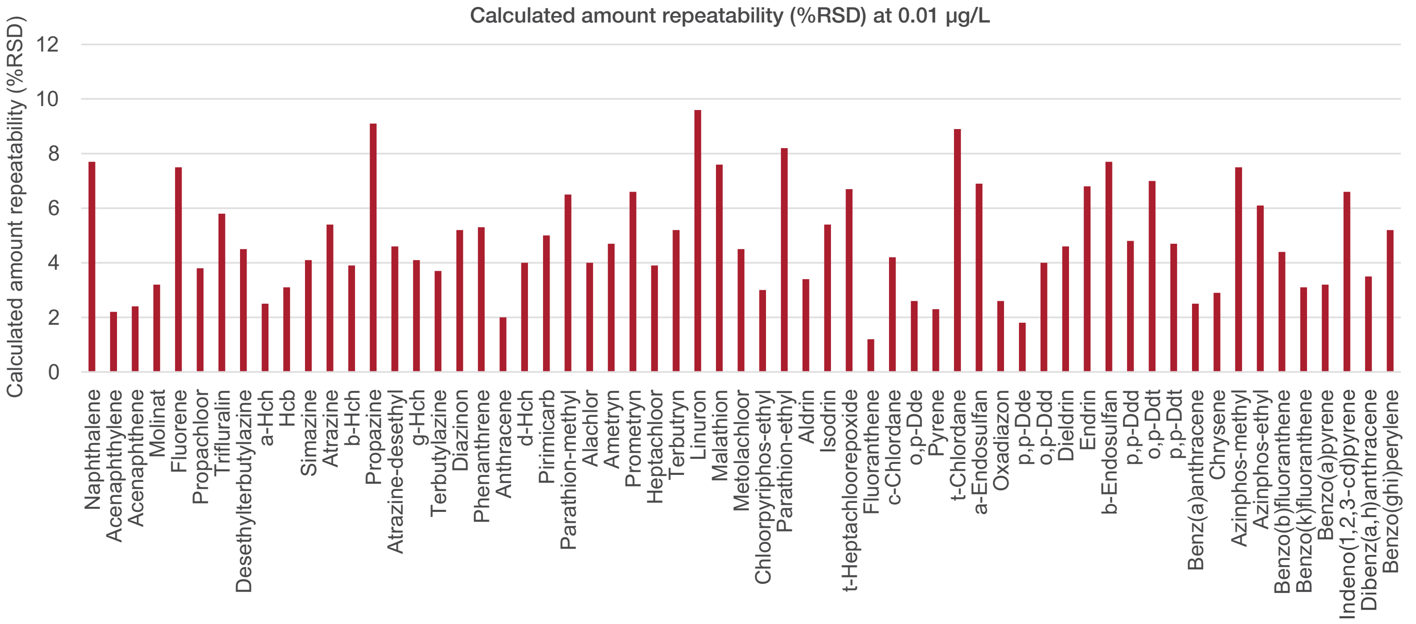


Figure 7. Calculated amount repeatability (%RSD) for n=10 calibration standards at 0.01 µg/L, submitted to the entire extraction workflow

Table 3. Examples of MDL calculation for some PAH compounds

Replicate	Benzo(*b*)fluoranthene (µg/L)	Benzo(*k*)fluoranthene (µg/L)	Indeno(*1,2,3-cd*)pyrene (µg/L)	Benzo(*ghi*)perylene (µg/L)	Benzo(*a*)pyrene (µg/L)
1	0.00116	0.00107	0.00099	0.00119	0.00080
2	0.00132	0.00117	0.00107	0.00123	0.00082
3	0.00114	0.00105	0.00101	0.00115	0.00079
4	0.00121	0.00106	0.00100	0.00115	0.00078
5	0.00122	0.00117	0.00106	0.00119	0.00079
6	0.00122	0.00102	0.00105	0.00121	0.00074
% RSD	**5.3**	**5.9**	**3.3**	**2.9**	**3.6**
MDL (µg/L)	**0.00021**	**0.00022**	**0.00011**	**0.00011**	**0.00009**

Table 4. The automated DLLME offered many advantages compared to manual sample preparation, allowing for reduced solvent consumption and waste as well as reduced costs for sample transportation and storage, optimization of labor time, and increased productivity.

	SPE + GCMS	Automated DLLME + LVI + GCMS/MS	Impact
Solvent consumption	Pesticides: 9 mL methanol + 1 mL DCM + 1 mL ethylacetate PAHs: 9 mL methanol + 3 mL DCM + 3 mL hexane + 0.5 mL ACN	0.4 mL DCM 0.9 mL methanol	Cost savings
Sample volume	Pesticides: 200 mL PAHs: 500 mL	5 mL	Smaller volumes and weights Reduced picking and transport costs
Analyst time	Batch 20 samples: Pesticides: 4 hours PAHs: 12 hours	30 minutes for all targets	Optimization of labor time
Samples / day	24	48 samples / day	Increased productivity
Manual processing residues	Many	Only few	Increased productivity

Conclusion

The TriPlus RSH SMART autosampler serving the TSQ 9610 GC-MS/MS with the AEI source was used to execute the automated DLLME workflow with on-line analysis for the determination of PAHs and pesticides in water samples. This automated approach was adopted as a replacement for the manual SPE protocol followed by off-line GC-MS analysis. The automated approach provided significant benefits in terms of time/cost savings and improved sensitivity:

- Automation allowed the adoption of DLLME to reduce solvent consumption while responding to increasing sample workload with faster turnaround time and unattended 24/7 operations.
- Automation allowed the use of DLLME in combination with highly sensitive GC-MS/MS analysis to stay compliant with stringent legislation requirements for drinking water while covering different matrix complexity with the same unattended workflow.
- The adopted automated workflow opens up to method consolidation, offering the possibility to add further target contaminants in the same analytical run.

References

1. Water Framework Directive (europa.eu)
2. UK Chemical Investigation Program Phase 2 (CIP2)
3. Thermo Scientific On-demand webinar – Cost savings and increased data quality through automation
4. www.sampleQ.com

Appendix

Table A1 (part 1). List of target compounds, including precursor and product masses as well as collision energies

Name	Retention time (RT, min)	Precursor mass (*m/z*)	Product mass (*m/z*)	Collision energy (eV)
1,4-Dichlorobenzene-d4	6.56	115	78	12
	6.56	149.9	78	28
	6.56	149.9	115	14
Naphthalene-d8	7.91	136	84.1	20
	7.91	136	108.1	18
	7.91	136	134.1	18
Naphthalene	7.93	128.1	102	17
	7.93	128.1	127	15
	7.93	128.1	78	20
2-Fluorobiphenyl	9.19	171.8	145.9	20
	9.19	171.8	150.7	25
	9.19	171.8	170	25
Acenaphthylene	9.79	152.1	126	23
	9.79	152.1	151.1	17
	9.79	152.1	102	26
Acenaphthene-d10	9.97	164.1	162.1	20
	9.97	164.1	160.1	30
Acenaphthene	10	153.1	152.1	18
	10	154.1	153.1	15
	10	154.1	152.1	16
Molinat	10.3	187.1	126.1	6
	10.3	187.1	98	8
	10.3	126.1	55	12
Fluorene	10.63	165.1	163.1	30
	10.63	166.1	164.1	32
	10.63	166.1	165.1	17
Propachlor	10.68	120.1	51	33
	10.68	120.1	77	17
	10.68	176.1	120	11
2,4,6-Tribromophenol	10.92	329.8	140.9	38
	10.92	329.8	221.6	20
	10.92	331.8	142.9	36
Trifluralin	10.99	306.1	264.1	7
	10.99	264.1	160.1	14
	10.99	264.1	206.1	7
Desethylterbutylazine	11.08	186	83	16
	11.08	201.1	145	10
	11.08	186	104	12
a-Hch	11.25	180.9	145	15
	11.25	216.9	180.9	9
	11.25	218.9	182.9	9
Hcb	11.3	283.8	213.9	30
	11.3	283.8	248.8	17
	11.3	285.8	250.8	17
Simazine	11.44	201.1	138.1	11
	11.44	201.1	173.1	7
	11.44	203.1	175.1	7
Atrazine	11.49	215.1	200.1	8
	11.49	200.1	122.1	9
	11.49	215.1	173.1	7
b-Hch	11.5	180.9	145	15
	11.5	216.9	180.9	9
	11.5	218.9	182.9	9

Table A1 (part 2). List of target compounds, including precursor and product masses as well as collision energies

Name	Retention time (RT, min)	Precursor mass (*m/z*)	Product mass (*m/z*)	Collision energy (eV)
Atrazine-desethyl	11.52	174.1	107.1	9
	11.52	187.1	58	13
	11.52	187.1	172.1	7
Propazine	11.52	172.1	104	11
	11.52	214.1	172.1	9
	11.52	229.1	214.1	8
g-Hch	11.61	182.9	109	27
	11.61	216.9	180.9	9
	11.61	218.9	182.9	9
Terbutylazine	11.64	173.1	172.1	9
	11.64	214.1	104	16
	11.64	214.1	132.1	9
Diazinon	11.69	248.1	137.1	15
	11.69	276.1	179.1	9
	11.69	304.1	179.1	10
Phenanthrene-d10	11.75	188	158.1	34
	11.75	188	160.1	20
	11.75	188	184.1	28
Phenanthrene	11.78	176.1	174.1	32
	11.78	178.1	176.1	27
	11.78	178.1	152.1	22
Anthracene	11.84	176.1	150.1	22
	11.84	178.1	176.1	27
	11.84	178.1	152.1	18
d-Hch	11.88	180.9	145	15
	11.88	216.9	180.9	9
	11.88	218.9	182.9	9
Pirimicarb	11.95	166.1	71	25
	11.95	166.1	96.1	10
	11.95	238.1	166.1	12
Parathion-methyl	12.26	263	109	11
	12.26	263	127	9
	12.26	263	246	6
Alachlor	12.28	160.1	132	9
	12.28	188.1	160.1	9
	12.28	237.1	160.1	9
Ametryn	12.34	227.1	170.1	11
	12.34	227.1	185.1	7
	12.34	227.1	212.1	9
Prometryn	12.37	226.1	184.1	9
	12.37	241.1	184.1	11
	12.37	241.1	226.1	9
Heptachlor	12.38	269.9	234.9	13
	12.38	271.9	236.9	13
	12.38	273.9	238.9	13

Name	Retention time (RT, min)	Precursor mass (*m/z*)	Product mass (*m/z*)	Collision energy (eV)
Terbutryn	12.5	170.1	128.1	9
	12.5	226.1	96.1	16
	12.5	241.1	170.1	13
Linuron	12.58	248.1	61	8
	12.58	250.1	61	15
	12.58	159.8	133	12
	12.58	187	124	20
Malathion	12.59	127	99	7
	12.59	173	99	14
	12.59	173	127	7
Metolachlor	12.66	238.1	133.1	26
	12.66	238.1	162.1	11
	12.66	240.1	162.1	11
Chlorpyriphos-ethyl	12.67	313.9	258	12
	12.67	197	169	12
	12.67	199	171	12
Parathion-ethyl	12.74	139	109	7
	12.74	155	125	8
	12.74	291	109	12
Aldrin	12.75	262.9	192.9	30
	12.75	262.9	227.9	20
	12.75	292.9	257.9	9
Pedimethalin	12.99	252.1	161	14
	12.99	252.1	162	8
	12.99	252.1	191.3	8
Isodrin	13.04	192.9	156.9	19
	13.04	194.9	158.9	19
	13.04	262.9	192.9	30
t-Heptachlorepoxide	13.17	216.9	146.9	32
	13.17	216.9	181.9	15
	13.17	236.9	143	21
Fluoranthene	13.22	202.1	152.1	32
	13.22	202.1	200.1	33
	13.22	203.1	201.1	32
c-Chlordane	13.36	372.8	263.9	20
	13.36	372.8	265.9	22
	13.36	374.8	265.9	20
o,p-Dde	13.36	246	175.9	30
	13.36	248	176	29
	13.36	317.9	246	18
Pyrene	13.48	200.1	199.1	17
	13.48	202.1	200.1	33
	13.48	203.1	201.1	36
a-Endosulfan	13.49	195	159.1	7
	13.49	240.9	205.9	12
	13.49	242.9	207.9	13
t-Chlordane	13.49	372.8	263.9	20
	13.49	372.8	265.9	22
	13.49	374.8	265.9	20

Table A1 (part 3). List of target compounds, including precursor and product masses as well as collision energies

Name	Retention time (RT, min)	Precursor mass (*m/z*)	Product mass (*m/z*)	Collision energy (eV)
Oxadiazon	13.65	175	112	12
	13.65	258.1	175	10
	13.65	175	76	28
p,*p*-Dde	13.67	246	175.9	30
	13.67	248	176	29
	13.67	317.9	246	18
p-Terphenyl-d14	13.73	244	226.2	20
	13.73	244	240.2	25
	13.73	244	242.2	15
o,*p*-Ddd	13.74	199	163	28
	13.74	234.9	165	22
	13.74	236.9	165	22
Dieldrin	13.76	262.9	192.9	30
	13.76	262.9	227.9	16
	13.76	276.9	240.9	9
Endrin	13.96	242.9	172.9	25
	13.96	262.9	192.9	30
	13.96	280.9	244.9	9
b-Endosulfan	14.05	194.9	158.9	8
	14.05	194.9	159.9	9
	14.05	240.9	205.9	12
p,*p*-Ddd	14.07	234.9	165	22
	14.07	234.9	199	13
	14.07	236.9	165	22
o,*p*-Ddt	14.11	234.9	165	22
	14.11	236.9	165	22
	14.11	234.9	199	13
p,*p*-Ddt	14.43	234.9	165	22
	14.43	234.9	199	13
	14.43	236.9	165	22
Benz(*a*)anthracene	14.94	226.1	224.1	35
	14.94	228.1	226.1	28
	14.94	228.1	224.1	60
Chrysene-d12	14.95	240.2	236.2	30
	14.95	240.2	212.1	30
Chrysene	14.98	228.1	224.1	60
	14.98	226.1	224.1	35
	14.98	228.1	226.1	28
Azinphos-methyl	15.24	132	77	12
	15.24	160	51	34
	15.24	160	77	16
Azinphos-ethyl	15.53	132	77	12
	15.53	160	51	34
	15.53	160	77	16
Benzo(*b*)fluoranthene	16.16	250.1	248.1	35
	16.16	252.1	250.1	33
	16.16	252.1	248.1	60
Benzo(*k*)fluoranthene	16.19	250.1	248.1	35
	16.19	252.1	250.1	33
	16.19	252.1	248.1	60
Benzo(*a*)pyrene	16.49	250.1	248.1	35
	16.49	252.1	250.1	10
	16.49	252.1	248.1	60
Perylene-d12	16.55	132.2	118.1	12
	16.55	260.1	256.1	34
	16.55	264.2	260.1	36
Indeno(*1,2,3-cd*)pyrene	17.59	274.1	272.1	37
	17.59	276.1	274.1	40
	17.59	276.1	272.1	60
Dibenz(*a*,*h*)anthracene	17.61	278.1	274.1	55
	17.61	278.1	276.1	30
	17.61	279.1	277.1	32
Benzo(*ghi*)perylene	17.87	138.1	137.1	17
	17.87	276.1	274.1	40
	17.87	276.1	275.1	23

Table A2 (part 1). Linearity ranges and calculated coefficient of determination (R^2) for the investigated PAHs and pesticides

Peak name	Lower limit (µg/L)	Upper limit (µg/L)	Coefficient of determination (R^2)	ISTD
Naphthalene	0.0005	1.0	0.998	Naphthalene-d8
Acenaphthylene	0.0005	1.0	1.000	Acenaphthene-d10
Acenaphthene	0.0005	1.0	1.000	Acenaphthene-d10
Molinat	0.0005	1.0	0.998	Acenaphthene-d10
Fluorene	0.0005	1.0	1.000	Acenaphthene-d10
Propachloor	0.0005	1.0	0.998	Acenaphthene-d10
Trifluralin	0.0005	1.0	1.000	Chrysene-d12
Desethylterbutylazine	0.0005	1.0	1.000	Chrysene-d12
a-Hch	0.0005	1.0	0.998	Acenaphthene-d10
Hcb	0.0005	1.0	0.998	Acenaphthene-d10
Simazine	0.0005	1.0	0.999	Chrysene-d12
Atrazine	0.0005	1.0	0.999	Chrysene-d12
b-Hch	0.0005	1.0	0.999	Chrysene-d12
Propazine	0.0005	1.0	0.999	Chrysene-d12
Atrazine-desethyl	0.01	1.0	0.999	Chrysene-d12
g-Hch	0.0005	1.0	0.999	Chrysene-d12
Terbutylazine	0.0005	1.0	0.999	Chrysene-d12
Diazinon	0.0005	1.0	0.999	Chrysene-d12
Phenanthrene	0.0005	1.0	1.000	Phenanthrene-d10
Anthracene	0.0005	1.0	1.000	Chrysene-d12
d-Hch	0.0005	1.0	0.999	Chrysene-d12
Pirimicarb	0.0005	1.0	1.000	Chrysene-d12
Parathion-methyl	0.0005	1.0	0.999	Chrysene-d12
Alachlor	0.0005	1.0	0.999	Chrysene-d12
Ametryn	0.0005	1.0	1.000	Chrysene-d12
Prometryn	0.0005	1.0	1.000	Chrysene-d12
Heptachloor	0.0005	1.0	1.000	Chrysene-d12
Terbutryn	0.0005	1.0	1.000	Chrysene-d12
Linuron	0.01	1.0	0.997	Chrysene-d12
Malathion	0.0005	1.0	1.000	Chrysene-d12
Metolachlor	0.0005	1.0	1.000	Chrysene-d12

Table A2 (part 2). Linearity ranges and calculated coefficient of determination (R^2) for the investigated PAHs and pesticides

Peak name	Lower limit (µg/L)	Upper limit (µg/L)	Coefficient of determination (R^2)	ISTD
Chloorpyriphos-ethyl	0.0005	1.0	1.000	Chrysene-d12
Parathion-ethyl	0.002	1.0	0.998	Chrysene-d12
Aldrin	0.0005	1.0	0.999	Chrysene-d12
Isodrin	0.0005	1.0	0.999	Chrysene-d12
t-Heptachlorepoxide	0.0005	1.0	0.999	Chrysene-d12
Fluoranthene	0.0005	1.0	1.000	Chrysene-d12
c-Chlordane	0.0005	1.0	1.000	Chrysene-d12
o,p-Dde	0.0005	1.0	0.998	Chrysene-d12
Pyrene	0.0005	1.0	1.000	Chrysene-d12
t-Chlordane	0.002	1.0	1.000	Chrysene-d12
a-Endosulfan	0.002	1.0	0.998	Chrysene-d12
Oxadiazon	0.0005	1.0	0.999	Chrysene-d12
p,p-Dde	0.0005	1.0	0.998	Chrysene-d12
o,p-Ddd	0.0005	1.0	1.000	Chrysene-d12
Dieldrin	0.002	1.0	0.999	Chrysene-d12
Endrin	0.002	1.0	1.000	Chrysene-d12
b-Endosulfan	0.0005	1.0	0.999	Chrysene-d12
p,p-Ddd	0.0005	1.0	1.000	Chrysene-d12
o,p-Ddt	0.0005	1.0	0.999	Chrysene-d12
p,p-Ddt	0.0005	1.0	0.999	Chrysene-d12
Benz(a)anthracene	0.0005	1.0	0.999	Chrysene-d12
Chrysene	0.0005	1.0	1.000	Chrysene-d12
Azinphos-methyl	0.0005	1.0	1.000	Chrysene-d12
Azinphos-ethyl	0.0005	1.0	1.000	Chrysene-d12
Benzo(*b*)fluoranthene	0.0005	1.0	0.997	Perylene-d12
Benzo(*k*)fluoranthene	0.0005	1.0	1.000	Perylene-d12
Benzo(*a*)pyrene	0.0005	1.0	0.999	Perylene-d12
Indeno(*1,2,3-cd*)pyrene	0.0005	1.0	0.997	Perylene-d12
Dibenz(*a,h*)anthracene	0.0005	1.0	0.996	Perylene-d12
Benzo(*ghi*)perylene	0.0005	1.0	0.997	Perylene-d12

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