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Environmental

Increasing throughput and sustainability in EPA Method 8270 for water analysis using automated LLE–GC-MS

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Keywords

EPA Method 8270, EPA Method 3511, water analysis, SVOC, automation, micro extraction, LLE, liquid-liquid extraction, greener chemistry

Goal

The purpose of this study is to validate an automated LLE–GC-MS workflow to deliver EPA Method 8270-quality analysis of SVOC in water with greener chemistry, faster results, and full regulatory confidence, with the possibility to extend target compounds list exceeding EPA Method 8270E requirements.

Introduction

Analyzing semi-volatile organic compounds (SVOCs) in water is a critical environmental task. U.S. EPA Method 8270 (SW-846) is the standard gas chromatography-mass spectrometry (GC-MS) protocol for detecting hundreds of SVOCs (pesticides, PCBs, PAHs, phenols, etc.) in environmental samples. Traditionally, EPA Method 8270 requires laborious liquid–liquid extraction (LLE) with large volumes of chlorinated solvents (e.g., dichloromethane, DCM), which is time-consuming and poses health and environmental hazards.[1,2,3] Within the extraction methods allowed for EPA Method 8270, EPA Method 3511 indicates a micro-extraction approach, suitable to be automatized due to the reduced volumes involved but still using dichloromethane as solvent.

Recent updates from the U.S. Environmental Protection Agency highlight the growing regulatory restrictions on methylene chloride under the *Toxic Substances Control Act (TSCA).* The 2024 EPA Guide to Complying with the *Methylene Chloride Regulation* details new prohibitions on many industrial and laboratory uses of DCM due to its significant risks to human health and the environment.[4] These changes underscore the urgent need for laboratories to adopt safer, compliant alternatives to chlorinated solvents in analytical workflows.

In this application note, we present a Thermo Fisher Scientific solution that fully automates the micro-LLE workflow for SVOC analysis in water samples, optimizing the extraction with ethyl acetate as solvent in place of DCM: a robotic autosampler performs the extraction steps and on-line injection into a triple quadrupole GC-MS/MS. This integrated system meets EPA Method 8270 performance criteria while dramatically improving throughput, safety, and sustainability.

Experimental

Instrumentation and method setup

GC-MS was performed using the Thermo Scientific™ TRACE™ 1610 Gas Chromatograph, coupled to the Thermo Scientific™ TSQ™ 9610 Triple Quadrupole MS. Chromatographic separation was achieved on the Thermo Scientific™ TraceGOLD™ TG-SVOC Capillary Column, 30 m × 0.25 µm × 0.25 mm ID (Cat. No. 26057-1420), specifically designed for a wide range of semivolatile organic compounds, ensuring excellent reproducibility and peak shapes even for challenging compounds such as phenol, nitrophenol, and pentachlorophenol. Table 1 contains the conditions and operating parameters for both GC and MS.

The Thermo Scientific™ TriPlus™ RSH SMART Autosampler was configured to perform a fully automated sample preparation, including calibration setup, internal standard (IS) and surrogates (SURR) addition, liquid-liquid extraction, and on-line injection (Figure 1). The detailed configuration of the robotic autosampler is listed in Appendix Table A1.

The Thermo Scientific™ TriPlus™ RSH Sampling Workflow Editor Software (Cat. No. 1R77010-1200) was utilized to program the entire sample preparation workflow. Once completed, the workflow was imported into the Thermo Scientific™ Chromeleon™ 7.4 Chromatography Data System (CDS) Software for execution. This integration ensures that the entire process—from sample preparation to acquisition and data processing—is fully automated and managed seamlessly within a single software platform, enhancing efficiency, consistency, and reliability for streamlined operations and reduced manual intervention.

Table 1. TRACE 1610 GC and TSQ 9610 MS parameters.

iConnect PTV injector				
Liner	Thermo Scientific™ LinerGOLD™ PTV 6-baffle liner (Cat. No. 453T2120)			
Injection volume (µL)	1			
Carrier gas flow (mL·min^{-1})	1.2			
Injection type	PTV splitless			
Splitless time (min)	1			
PTV ramp settings	Rate (°C·min^{-1})	Temp. (°C)	Time (min)	Flow (mL·min^{-1})
Injection phase	-	60	0.1	-
Transfer phase	10	300	1	-
Cleaning phase	14.5	320	5	50
Injection depth (mm)	42			
Column	TraceGOLD TG-SVOC 30 m × 0.25 µm × 0.25 mm (Cat. No. 26057-1420)			
GC oven temperature program				
Initial temperature (°C)	40			
Hold time (min)	1			
Rate 1 (°C·min^{-1})	10 (0 min)			
Temperature 1 (°C)	140			
Rate 2 (°C·min^{-1})	15			
Temperature 2 (°C)	250 (5 min)			
Rate 3 (°C·min^{-1})	15			
Temperature 3 (°C)	320			
Final temperature hold time (min)	5			
Total analysis time (min)	33			
TSQ 9610 MS with Thermo Scientific™ ExtractaBrite™ Source				
Transfer line (°C)	280			
EI Ion source temperature (°C)	320			
Electron energy (eV)	70			
Acquisition mode	Timed SRM			
Emission current (µA)	50			
Collision gas and pressure (psi)	Argon, 70			

Standards and sample preparation

The automated workflow used in this study includes the preparation of 12 calibration levels. Five commercially available standard mixtures from Restek™ were used for this work: Standard MegaMix™ 8270 (Cat. No. 31850), Organophosphorus Pesticide Mix, 8270/Appendix IX (Cat. No. 32419), GC Multiresidue Pesticide Standard #2 (Cat. No. 32564), GC Multiresidue Pesticide Standard #5 (Cat. No. 32567), and GC Multiresidue Pesticide Standard #6 (Cat. No. 32568).

Figure 1. TriPlus RSH SMART autosampler configuration for automated LLE workflow for SVOC in water according to EPA Method 8270. (A) Standard washing station (5 × 10 mL vials). (B) Vial trays. (C) Vortexer. (D) Fast washing station. (E) Automatic tool change (ATC).

Two stock solutions were manually prepared in methanol starting from the commercial standard mixtures, one containing the analytes of the MegaMix 8270 at a concentration of 100 mg/L (ppm) and one containing 99 pesticides (OCPs, ONPs, OPPs, and pyrethroids) at a concentration of 10 mg/L (ppm). These stock solutions were placed in the rack designated for 2 mL vials (VT54), as illustrated in Figure 2, and automatically diluted 1/100 in methanol, thus obtaining a final set of four calibration working solutions:

- EPA 8270 at 100 mg/L (STD A high)
- EPA 8270 at 1 mg/L (STD A low)
- Pesticides mix at 10 mg/L (STD B high)
- Pesticides mix at 0.1 mg/L (STD B low)

Additionally, a mixture of the EPA Method 8270 acid, basic, and neutral surrogates (Restek B/N Surrogate Mix and Acid Surrogate Mix, Cat. No. 31024 and 31025) at 5 mg/L in methanol and the EPA Method 8270 Internal Standard (Restek Internal Standard Mix, Cat. No. 31206) solution at 5 mg/L in ethyl acetate were manually prepared and positioned on the same VT54 rack (Figure 2).

The workflow is flexible regarding the vial capacity and the rack position for standards mixtures to accommodate sample throughput as needed. Quality control samples may also be added to the workflow to check the method performance in the daily routine. Separate levels or separate standard solution may be used for such purposes.

The calibration levels were prepared starting from 10 mL of MilliQ™ water placed in 20 mL vials, where aliquots of standard mixtures spanning from 1 to 50 µL were automatically added to cover a calibration range from 0.01 µg/L (ppb) to 50 µg/L for pesticides and 0.1 µg/L to 500 µg/L for the EPA Method 8270 mix.

To provide a consistent organic layer and to boost the extraction yield, 1 g of salt (50:50 mixture of NaCl and $MgSO_4$) was added to each calibration vial before adding the MilliQ water and to each sample vial before filling with 10 mL of water sample.

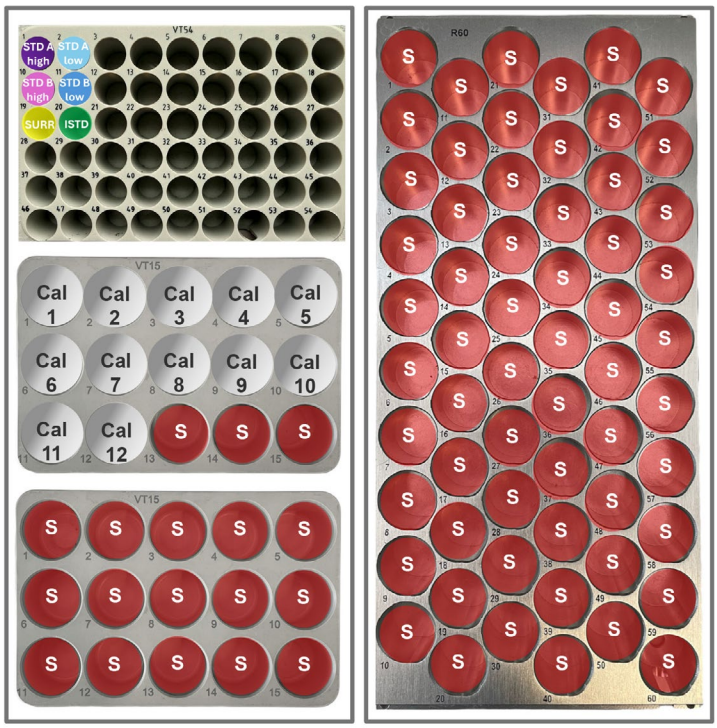
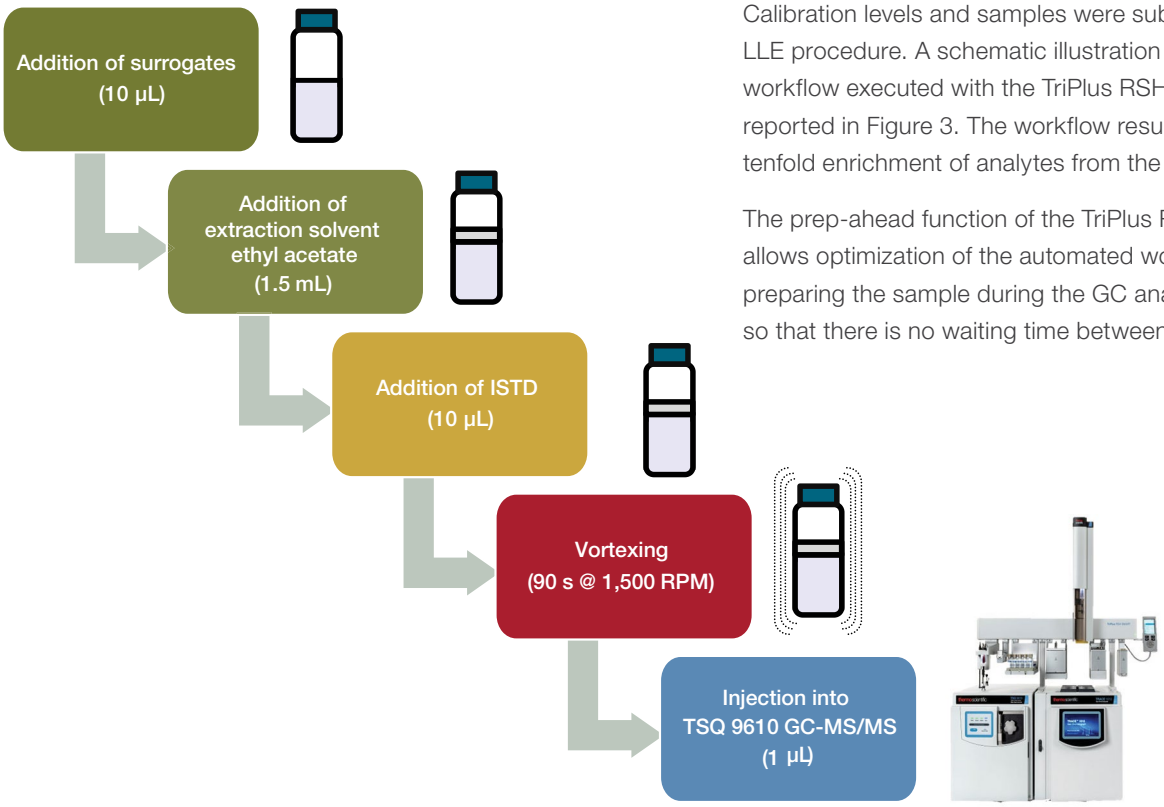


Figure 2. Schematic of standards and sample vial positions on the TriPlus RSH SMART vial trays, as used in this study.



Calibration levels and samples were submitted to the same LLE procedure. A schematic illustration of the automated LLE workflow executed with the TriPlus RSH SMART autosampler is reported in Figure 3. The workflow results in an approximately tenfold enrichment of analytes from the water sample.

The prep-ahead function of the TriPlus RSH SMART autosampler allows optimization of the automated workflow cycle time by preparing the sample during the GC analysis of the previous one, so that there is no waiting time between two injections.

Figure 3. Automated LLE workflow executed for calibration standards and samples.

Results and discussion

A total of 173 analytes were included in the calibration standards, covering different classes of SVOC, exceeding EPA Method 8270 requirements. The full list of target analytes is reported in Appendix Table A2, along with the SRM transitions.

Calibration

Depending on the analytes, the calibration curves included 4 (only for 4,6-dinitro-2-methylphenol) to 12 concentration levels to cover a range of up to more than 3 orders of magnitude. Most of the analytes (about 70% of them) showed a good correlation over 10 to 12 calibration levels. Due to the wide concentration range covered, a quadratic fitting was used for some analytes. Calibration curves at narrower concentration ranges or a different ISTD concentration may be chosen to stay in the linear range. Coefficient of determination (R^2) and RSD% of the calibration response are listed for each analyte in Table A3 in the Appendix. The R^2 (linear or quadratic) is >0.99 for most of the analytes and the RSD% is lower than 20%, in compliance with the EPA Method 8270E guideline. The internal standard response variation is also within the ranges required by the method (within 50% to 200% of midpoint of ICAL), as well as the RT tolerance (±10 s).

An example of a chromatogram for a mid-level calibration standard is reported in Figure 4, while examples of calibration curves are shown in Figures 5A and 5B for selected compounds.

Limits of quantitation (LOQ)

The lowest point in the initial calibration ICAL was chosen as the LLOQ (lowest calibration level) of the method (refer to the Table A3 in the Appendix). The choice of the LLOQ was based on the criteria stated in the EPA Method 8270E guideline based on accuracy, linearity, and RF RSD%.[1] The lowest calibration point for the 8270 MegaMix solution of 0.1 µg/L in water was used for 40 analytes out of the 74. The other compounds had LLOQ lower than 3.5 µg/L. Only the 4,6-dinitro-2-methylphenol showed an LLOQ as high as 50 µg/L. For the pesticides mix, 25 compounds out of the 99 met the LLOQ at 0.05 µg/L. These results demonstrated a good sensitivity of the method due to the excellent extraction yield of the ethyl acetate for the compounds under study, combined with the analytical performance of the TSQ 9610 GC-MS.

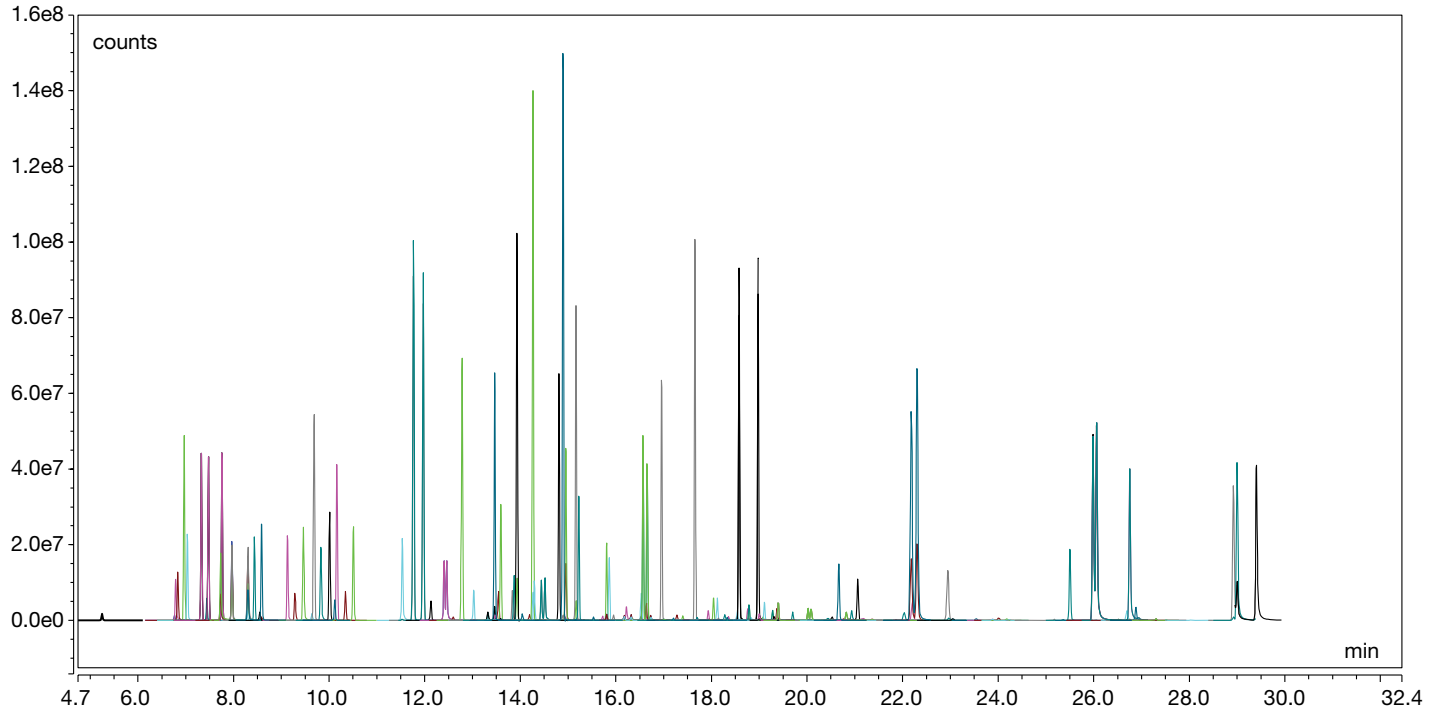


Figure 4. SRM chromatogram of a mid-level calibration standard.

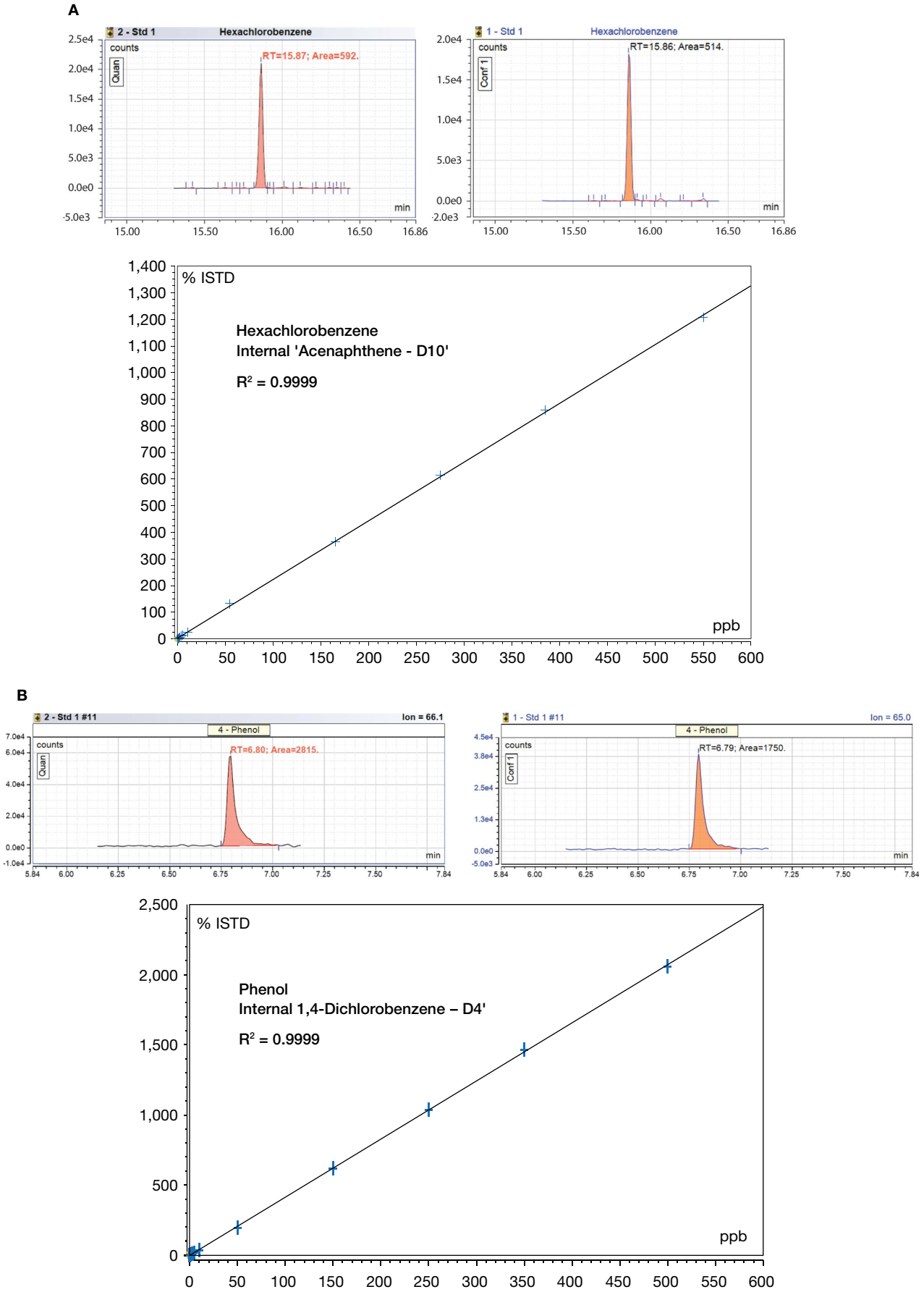


Figure 5. Internal standard calibration. (A) Hexachlorobenzene, 1 µL injection, full range, extracted ions from level 1 (0.1 µg/L). (B) Phenol, 1 µL injection, full range, extracted ions from level 1 (0.5 µg/L).

Particular attention must be paid to the use of ethyl acetate as extraction solvent, due to its affinity for water. The moisture in the extraction solvent may affect the sensitivity at low concentrations, especially for the more polar compounds, during the daily routine. The ethyl acetate is water soluble, and the organic layer is mostly dependent on the salt quantity added to the water as well as to the total volume of the solvent itself. By optimizing these two parameters, it is possible to control and reduce the moisture in the organic layer. A Restek™ Hydroguard™ pre-column may be used to protect the analytical column from moisture or an automated drying process in pre-filled 2 mL vial with Na_2SO_4 can be implemented in the automated workflow. Nevertheless, even without those precautions, more critical analytes such as aniline or more acidic compounds started to show tailing or signal loss due to surfaces activation after more than 200 LLE injections (1 and 10 µL) without any column trimming or column replacement. These results showed a good stability and robustness of the TraceGOLD TG-SVOC column chosen for the study.

Repeatability

Automated LLE workflow repeatability was assessed on six replicates of the three lower calibration levels. The areas of the analytes included in those calibration levels and their RSD% were evaluated to assess the precision of the spiking and extraction procedures. Except for seven analytes, the RSD% for all the analytes was lower than 15%, showing a good repeatability of the workflow even at very low spiked concentrations. The results are shown in Table A4 in the Appendix.

Blanks

Blanks were checked every 10 samples automatically by spiking SURR and ISTD in 10 mL of MilliQ water with the salt addition as a normal sample analysis procedure. Blanks levels are in line with the requirements of the EPA Method 8270E. The use of the solvent addition through the Fast Wash Station ensures fresh solvent for each extraction, avoiding any possible cross contamination between the samples. In case of taking the extraction solvent from vials, an automated matrix subtraction can be implemented in Chromeleon CDS to remove possible phthalate contamination (mostly diethyl phthalate and di-*n*-butyl phthalate) from the vial septa.

Large volume approach

A key benefit of using a PTV injector is the flexibility to move from standard to large volume injections, if lower limits of detection are required, as reported in a previous application note[6] for the analysis of SVOC in drinking water. By using a sintered liner and a solvent split injection mode, it is possible to inject tens of microliters with a significant increase in sensitivity. The 6-baffled liner used in this study permits the large volume injections of usually no more than 10 µL in splitless mode. Large volume injection offers in this case the opportunity to decrease the LOQs without changing the instrument configuration. The PTV large volume splitless method is shown in Table 2, while the GC oven program and MS method remained unchanged. A 50 µL cone tip syringe was used to perform the injection. Linearity and repeatability were evaluated by injecting 10 µL over the six lower calibration levels.

Table 2. PTV Large Volume injection method.

iConnect PTV injector				
Liner	Thermo Scientific™ LinerGOLD™ PTV 6-baffle liner (Cat. No. 453T2120)			
Injection volume (µL)	10			
Carrier gas flow (mL·min^{-1})	1.2			
Injection type	PTV Large Volume (splitless)			
Splitless time (min)	1			
PTV ramp settings	Rate (°C·min^{-1})	Temp. (°C)	Time (min)	Flow (mL·min^{-1})
Injection phase	-	45	0.2	70
Transfer phase	5	300	1	-
Cleaning phase	14.5	320	10	50
Injector penetration depth (mm)	40			
Injection speed (µL/s)	2			

Table A5 in the Appendix shows a representative example of the calibration curves obtained by injecting 10 µL of some analytes feasible at the lower calibration points. The results were plotted in External mode, without any internal standard ratio to correct any possible injection or extraction defect. The R^2 obtained were higher than 0.99, showing excellent injection repeatability and linearity even in a large volume injection. This approach allows a decrease in the detection limit of about one order of magnitude (analyte dependent) without replacing the liner. The solvent re-focusing effect into the column helps with polar compounds that tend to tail in the presence of active site. An example is reported in Figure 6, which shows the external calibration curve for pentachlorophenol from 0.1 to 5 µg/L in water obtained by injecting 10 µL, while the first calibration point (LOQ) for a 1 µL injection was 3.5 µg/L. The figure also shows the good peak shape of the extracted ion for the first concentration level.

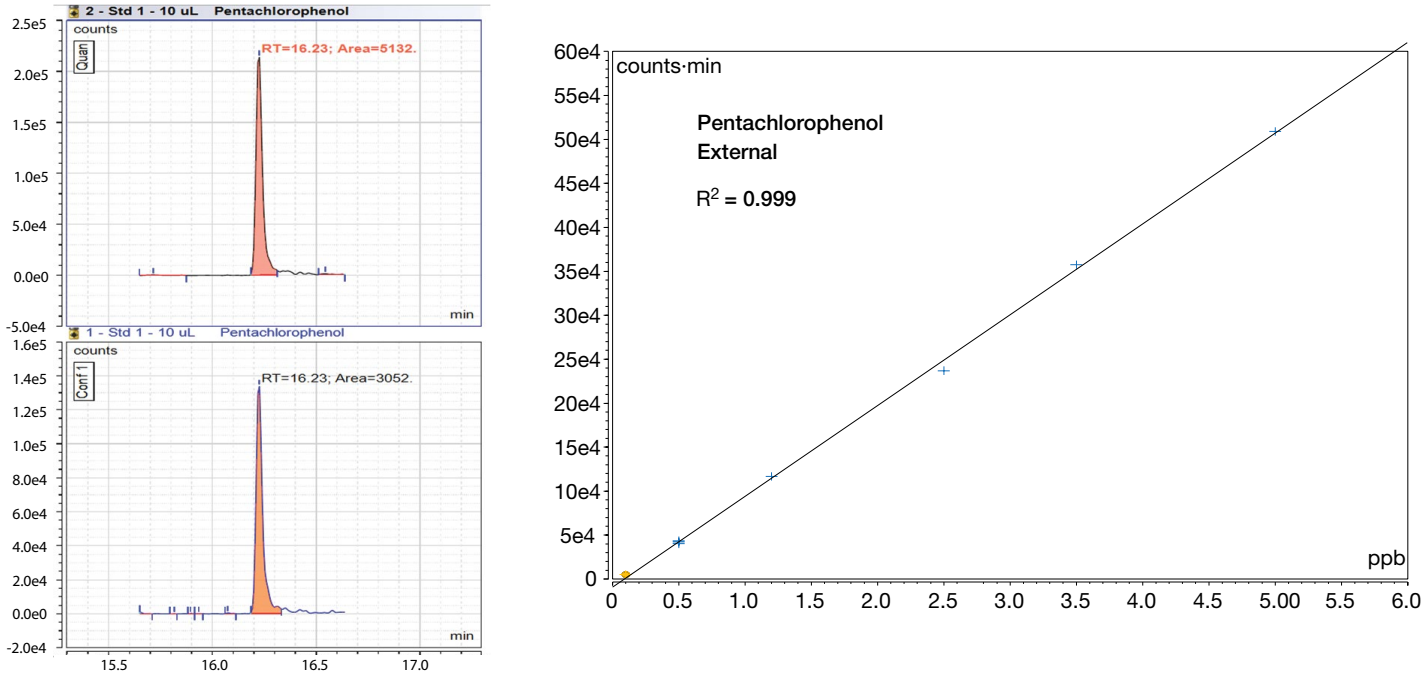


Figure 6. External standard calibration for pentachlorophenol, 10 µL injection, lower range. Extracted ions from level 1 (0.1 µg/L).

Benefits of automated EPA Method 8270 workflow

Implementing automation and miniaturization of sample and solvent volumes provides several benefits to modern laboratories:

- **Greener chemistry:** In line with the new EPA directives, the automated micro-LLE protocol eliminates the use of dichloromethane and replaces it with a less hazardous solvent, removing operator exposure and reducing environmental impact. Additionally, by scaling the extraction down to microliter volumes, solvent waste and cost are minimized.[5] This miniaturized workflow embodies greener chemistry without sacrificing extraction efficiency.
- **Automation for throughput:** A Thermo Scientific TriPlus RSH SMART autosampler executes every step of the LLE procedure automatically. Full automation removes manual pipetting and separatory funnel handling, delivering substantial time and labor savings. The results are consistently reproducible extractions and a much higher sample throughput. Laboratories can run unattended sample batches with confidence, freeing analysts to focus on data review rather than sample prep.
- **EPA Method 8270 compliance and flexibility:** The presented workflow is fully compliant with EPA Method 8270 requirements for SVOC analysis, as well as in line with the micro-extraction EPA Method 3511. The triple-quadrupole GC–MS/MS achieves high sensitivity, stability, and full QC demanded by the method. In addition, the flexibility of the system allows the target analyte list to be easily expanded. New SVOCs or emerging contaminants can be added to the GC–MS/MS method without changing the core automated protocol. By combining advanced MS detection and automation, this solution ensures efficient, regulation-compliant analysis.

Conclusions

An automated workflow solution for the analysis of SVOCs in water samples in compliance with the EPA Method 8270E was designed and validated, offering a reliable, user-friendly, sensitive, and greener method. The automated sample preparation allows a testing laboratory to increase the daily sample throughput while maintaining a high level of confidence in the results and decreasing the cost of each analysis. The combination of a greener solvent like ethyl acetate in place of dichloromethane, known to be a carcinogenic compound, guarantees a safer environment for the technician working in a daily routine. Less solvent usage, less waste, and less sample volume are also in line with the "greener chemistry" guidelines, ensuring a healthier impact on the environment. The large volume injection approach is an option for the user to decrease the LOQs when needed, maintaining the same instrument configuration used for 1–2 µL split or splitless injections of the daily routine.

References

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5. Thermo Fisher Scientific Application Note 003270: Automated dispersive liquid-liquid micro extraction (DLLME) for GC-MS/MS analysis of semi-volatile compounds in water. https://documents.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-003270-gc-autosampler-triplusrsh-svoc-an003270-na-en.pdf
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Appendix

Table A1. TriPlus RSH SMART autosampler configuration: tools and consumables.

TriPlus RSH SMART autosampler	Cat. No.
TriPlus RSH SMART autosampler, Advanced for liquid injection, regular rail length, including:	1R77010-2003
• 1× Liquid syringe tool for 0.5–100 µL syringes, 57-mm needle length	1R77010-1007
• 1× Tray holder	1R77010-1021
• 3× VT54 trays, for 54 vials of 2 mL	1R77010-1023
• 1× Standard washing station with 5 × 10 mL vials	1R77010-1023
Automatic Tool Change (ATC) module	1R77010-1019
Liquid syringe tool for 0.5–100 µL syringes, 57-mm needle length	1R77010-1007
Liquid syringe tool for 250–1,000 µL syringes, 57-mm needle length	1R77010-1009
Tray holder	1R77010-1021
R60 aluminium vial tray for 60 vials of 10/20 mL	1R77010-1025
2× VT15 trays for 15 vials of 10/20 mL	1R77010-1022
Fast washing module for two solvents	1R77010-1098
Vortexer module	1R77010-1033
Consumables	**Cat. No.**
Thermo Scientific™ GC SMART Syringe, 10 µL fixed needle, 26s gauge, 57 mm length	365D0291-SM
Thermo Scientific™ GC SMART Syringe, 50 µL fixed needle, gas-tight, 23s gauge, 57 mm length with side hole	365G2311-SM
Thermo Scientific™ GC SMART Syringe, 1,000 µL fixed needle, gas-tight, 22 gauge, 57 mm length	365K2811-SM
Headspace vial, 20 mL clear screw glass, 100/pack	6ASV20-1
Headspace vial cap, silver magnetic screw (18 mm) with silicone (blue)/PTFE seal	6PMSC18-ST2
Vial, 2 mL clear screw glass (9 mm short thread) with write-on patch, Performance Level 2, 100/Pack	6ASV9-1P
Cap, blue screw (9 mm) (PP: white silicone/red PTFE septa: 1.0 mm thickness) with AVCS technology, Performance Level 2, 100/Pack	6ASC9ST1
Software	**Cat. No.**
Sampling Workflow Editor software	1R77010-1200

Table A2 (part 1). Selected reaction monitoring (SRM) transitions for data acquisition by GC-MS/MS.

Name	RT	Window	Mass	Product mass	Collision energy
2-Fluorophenol (SURR)	5.2	1	112	63	24
2-Fluorophenol (SURR)	5.2	1	112	63.7	14
Phenol-d6 (SURR)	6.7	1	99.1	69.1	18
Phenol-d6 (SURR)	6.7	1	99.1	71	10
Phenol	6.7	1	93.6	65	16
Phenol	6.7	1	93.6	66.1	10
Aniline	6.7	1	93	65	20
Aniline	6.7	1	93	65.8	12
Bis(2-chloroethyl)ether	6.9	1	93	63	6
Bis(2-chloroethyl)ether	6.9	1	94.9	65	6
2-Chlorophenol	6.9	1	128	62.9	24
2-Chlorophenol	6.9	1	128	64.2	16
1,3-Dichlorobenzene	7.2	1	146	74.7	26
1,3-Dichlorobenzene	7.2	1	146	111	14
1,4-Dichlorobenzene-d4 (ISTD)	7.4	1	149.9	78	28
1,4-Dichlorobenzene-d4 (ISTD)	7.4	1	149.9	115	14
1,4-Dichlorobenzene	7.4	1	146	74.6	26
1,4-Dichlorobenzene	7.4	1	146	111	14
1,2-Dichlorobenzene	7.7	1	146	74.7	26
1,2-Dichlorobenzene	7.7	1	146	111	14
Benzyl alcohol	7.8	1	107.1	77	18
Benzyl alcohol	7.8	1	108.1	107	8
2-Methylphenol	7.9	1	107.1	77	18
2-Methylphenol	7.9	1	108.1	77	24
2,2'-Oxybis (1-chloropropane)	8	1	77	51	14
2,2'-Oxybis(1-chloropropane)	8	1	79	77	10
N-Nitroso-di-n-propylamine	8.3	1	70.1	41	12
N-Nitroso-di-n-propylamine	8.3	1	70.1	42.7	6
3+4-Methylphenol	8.3	1	107.1	77	18
3+4-Methylphenol	8.3	1	108.1	107.1	14
Hexachloroethane	8.4	1	117	81.9	28
Hexachloroethane	8.4	1	200.9	165.8	14
Nitrobenzene-d5 (SURR)	8.5	1	82.1	54	15
Nitrobenzene-d5 (SURR)	8.5	1	128.1	82	10
Nitrobenzene	8.6	1	77	50.9	12
Nitrobenzene	8.6	1	123.1	77	12
Isophorone	9.1	1	82.1	39	12
Isophorone	9.1	1	82.1	54.1	6
2-Nitrophenol	9.3	1	139.1	81	12
2-Nitrophenol	9.3	1	139.1	109	8
2,4-Dimethylphenol	9.4	1	107.1	77	14
2,4-Dimethylphenol	9.4	1	122.1	107	12
O,O,O-Triethyl thiophosphate	9.6	1	121	65	8
O,O,O-Triethyl thiophosphate	9.6	1	198	114	12
Bis(2-chloroethoxy) methane	9.7	1	93	63	6
Bis(2-chloroethoxy)methane	9.7	1	94.9	65	6
2,4-Dichlorophenol	9.8	1	163.9	63	26
2,4-Dichlorophenol	9.8	1	162	62.9	26
1,2,4-Trichlorobenzene	10	1	180	109	24
1,2,4-Trichlorobenzene	10	1	180	144.9	14
Naphthalene-d8 (ISTD)	10	1	136	108.1	18
Naphthalene-d8 (ISTD)	10	1	136	134.1	18
Naphthalene	10.1	1	128	102	18
Naphthalene	10.1	1	128	126.9	16
4-Chloroaniline	10.3	1	91.9	65	8
4-Chloroaniline	10.3	1	128.8	65.1	22
Hexachlorobutadiene	10.5	1	222.9	187.9	14
Hexachlorobutadiene	10.5	1	224.9	189.9	14
4-Chloro-3-methylphenol	11.5	1	107.1	77	12
4-Chloro-3-methylphenol	11.5	1	142.1	107	12
2-Methylnaphthalene	11.8	1	141.7	115	28
2-Methylnaphthalene	11.8	1	141.7	141.1	14
1-Methylnaphthalene	12	1	142.1	115	30
1-Methylnaphthalene	12	1	142.1	141.1	14
Hexachloro-cyclopentadiene	12.1	1	234.9	140.9	22
Hexachloro-cyclopentadiene	12.1	1	236.8	142.9	24
2,4,6-Trichlorophenol	12.4	1	132	97	10
2,4,6-Trichlorophenol	12.4	1	196	97	28
2,4,5-Trichlorophenol	12.4	1	196	97	28
2,4,5-Trichlorophenol	12.4	1	197.9	97	28
2-Fluorobiphenyl (SURR)	12.6	1	171.8	150.7	25
2-Fluorobiphenyl (SURR)	12.6	1	171.8	170	25
2-Chloronaphthalene	12.8	1	162.1	77	32
2-Chloronaphthalene	12.8	1	162.1	126.9	18
2-Nitroaniline	13	1	92	65	8
2-Nitroaniline	13	1	138.1	92	12
4-Nitrophenol	13	1	139.1	81	14
4-Nitrophenol	13	1	139.1	109	8
1,4-Dinitrobenzene	13.3	1	92.1	63	12
1,4-Dinitrobenzene	13.3	1	168.1	75.1	26
1,3-Dinitrobenzene	13.5	1	122	75.1	12
1,3-Dinitrobenzene	13.5	1	168.1	75	24
Dimethyl phthalate	13.5	1	163.1	77	20
Dimethyl phthalate	13.5	1	163.1	133	8
Etridiazole	13.5	1	182.8	139.9	14
Etridiazole	13.5	1	211	182.9	10
2,6-Dinitrotoluene	13.5	1	165	63	20
2,6-Dinitrotoluene	13.5	1	165	148	8
Acenaphthylene	13.6	1	151.9	125.8	24
Acenaphthylene	13.6	1	151.9	150	28
1,2-Dinitrobenzene	13.6	1	168.1	52.8	32
1,2-Dinitrobenzene	13.6	1	168.1	63.2	38
Acenaphthene-d10 (ISTD)	13.8	1	162.1	160.1	18
Acenaphthene-d10 (ISTD)	13.8	1	164	162.1	16

Table A2 (part 2). Selected reaction monitoring (SRM) transitions for data acquisition by GC-MS/MS.

Name	RT	Window	Mass	Product mass	Collision energy
3-Nitroaniline	13.8	1	138.2	65	22
3-Nitroaniline	13.8	1	138.2	92	12
Acenaphthene	13.9	1	152.8	152.2	18
Acenaphthene	13.9	1	154.1	153.1	16
Chloroneb	14	1	190.9	113	14
Chloroneb	14	1	206	190.9	12
2,4-Dinitrophenol	14.1	1	184	79	10
2,4-Dinitrophenol	14.1	1	184	184	5
2,4-Dinitrophenol	14.1	1	184.1	107	10
2,4-Dinitrophenol	14.1	1	184.1	154	6
Pentachlorobenzene	14.2	1	249.8	143.6	38
Pentachlorobenzene	14.2	1	249.8	214.8	16
Dibenzofuran	14.3	1	168.1	139	24
Dibenzofuran	14.3	1	169.1	139.9	24
2,4-Dinitrotoluene	14.3	1	89.1	63	12
2,4-Dinitrotoluene	14.3	1	165.1	118.9	6
2,3,5,6-Tetrachlorophenol	14.4	1	229.9	130.9	26
2,3,5,6-Tetrachlorophenol	14.4	1	231.9	132.9	28
2,3,4,6-Tetrachlorophenol	14.5	1	229.9	130.9	26
2,3,4,6-Tetrachlorophenol	14.5	1	233.8	132.9	26
Diethyl Phthalate	14.8	1	149.1	65.1	20
Diethyl Phthalate	14.8	1	177.1	149	8
Fluorene	14.9	1	165	163	30
Fluorene	14.9	1	166.1	165.1	16
Thionazin	14.9	1	142.9	52	22
Thionazin	14.9	1	142.9	79	10
4-Nitroaniline	14.9	1	108.1	80	10
4-Nitroaniline	14.9	1	138.1	108	8
4-Chlorophenyl phenyl ether	14.9	1	141.1	115	14
4-Chlorophenyl phenyl ether	14.9	1	204.1	141.1	14
4,6-Dinitro-2-methylphenol	15.1	1	198.1	121	10
4,6-Dinitro-2-methylphenol	15.1	1	198.1	168.1	6
Diphenylamine	15.2	1	168.1	167.1	14
Diphenylamine	15.2	1	169.2	167.1	22
Azobenzene	15.2	1	105.1	77	6
Azobenzene	15.2	1	182.1	77	14
2,4,6-tribromophenol (SURR)	15.3	1	329.8	140.9	38
2,4,6-tribromophenol (SURR)	15.3	1	331.8	142.9	36
Sulfotep	15.5	1	202	145.9	10
Sulfotep	15.5	1	265.9	145.9	15
Phorate	15.7	1	75	47	8
Phorate	15.7	1	121	65	8
BHC, Alpha	15.8	1	182.8	146.7	12
BHC, Alpha	15.8	1	218.8	183	8
4-Bromophenyl phenyl ether	15.8	1	248	141.1	16
4-Bromophenyl phenyl ether	15.8	1	249.9	141.1	16
Hexachlorobenzene	15.9	1	283.8	213.8	22
Hexachlorobenzene	15.9	1	283.8	248.8	12
Pentachloroanisole	15.9	1	266.8	238.9	18
Pentachloroanisole	15.9	1	279.9	236.9	16
Dimethoate	16	1	87	42.1	14
Dimethoate	16	1	93	63	12
Atrazine	16.1	1	200	122.1	10
Atrazine	16.1	1	215.1	58.1	5
BHC, Beta	16.2	1	180.9	145	10
BHC, Beta	16.2	1	218.7	183	6
Pentachlorophenol	16.2	1	263.9	164.9	38
Pentachlorophenol	16.2	1	267.8	166.9	16
BHC, Gamma	16.3	1	180.9	145	24
BHC, Gamma	16.3	1	218.7	183	24
Terbuthylazine	16.4	1	214.1	104	12
Terbuthylazine	16.4	1	214.1	132	6
Phenanthrene-d10 (ISTD)	16.4	1	188	158.1	26
Phenanthrene-d10 (ISTD)	16.4	1	188	160.1	28
Pyrimethanil	16.5	1	198.1	117.9	26
Pyrimethanil	16.5	1	198.1	182.9	26
Phenanthrene	16.6	1	178	150.9	20
Phenanthrene	16.6	1	178	151.6	8
Terbacil	16.6	1	160	117	30
Terbacil	16.6	1	161.2	144	16
Disulfoton	16.6	1	88	45	22
Disulfoton	16.6	1	88	59.8	10
Tefluthrine	16.6	1	177	127	10
Tefluthrine	16.6	1	197	141	8
Anthracene	16.7	1	178	151	14
Anthracene	16.7	1	178	151.7	14
BHC delta	16.7	1	182.8	146.7	10
BHC delta	16.7	1	218.8	182.9	6
Carbazole	16.9	1	167.2	139	14
Carbazole	16.9	1	167.2	166.1	22
Endosulfan ether	17	1	69	41.1	6
Endosulfan ether	17	1	240.9	206	14
Vinclozoline	17.2	1	186.8	124	38
Vinclozoline	17.2	1	198	145	36
Methyl parathion	17.2	1	124.9	79	10
Methyl parathion	17.2	1	263	109	15
Transfluthrin	17.3	1	163	91.1	8
Transfluthrin	17.3	1	163	143	8
Heptachlor	17.4	1	99.8	65	12
Heptachlor	17.4	1	271.8	236.9	8
Di-n-butyl phthalate	17.7	1	149.1	65	16
Di-n-butyl phthalate	17.7	1	149.1	93	16
Pentachlorothioanisole	17.7	1	295.7	245.9	
Pentachlorothioanisole	17.7	1	295.7	262.9	

Table A2 (part 3). Selected reaction monitoring (SRM) transitions for data acquisition by GC-MS/MS.

Name	RT	Window	Mass	Product mass	Collision energy
Parathion (ethyl parathion)	17.9	1	109	81	10
Parathion (ethyl parathion)	17.9	1	124.9	97	6
Aldrin	17.9	1	262.7	191	30
Aldrin	17.9	1	262.7	192.9	32
Antraquinone	17.9	1	180.1	152	12
Antraquinone	17.9	1	208.1	152	22
4,4'-Dichlorobenzophenone	18	1	139	74.9	26
4,4'-Dichlorobenzophenone	18	1	139	111	12
Fenson	18.1	1	77	51	14
Fenson	18.1	1	141	77	8
MGK-264	18.1	1	164	93.1	10
MGK-264	18.1	1	164	98.1	10
Cyprodinil	18.3	1	224.1	196.9	20
Cyprodinil	18.3	1	224.1	208	18
Fipronil	18.3	1	366.9	212.9	28
Fipronil	18.3	1	368.8	214.9	30
Isodrin	18.3	1	146.8	111.1	10
Isodrin	18.3	1	192.9	123	28
Penconazole	18.4	1	158.9	89	28
Penconazole	18.4	1	248	157	22
Bioallethrin	18.4	1	107	79	6
Bioallethrin	18.4	1	123.1	41.1	24
Heptachlor epoxide	18.4	1	352.8	262.9	16
Heptachlor epoxide	18.4	1	354.7	264.9	12
Procymidone	18.5	1	95.9	53	16
Procymidone	18.5	1	95.9	67.1	8
Trifumizole	18.5	1	206	179	14
Trifumizole	18.5	1	206	186	8
Fluoranthene	18.6	1	202	152.1	30
Fluoranthene	18.6	1	202	200	32
Captan	18.6	1	117	82	30
Captan	18.6	1	151	79	14
Captan	18.6	1	151	80	6
Folpet	18.6	1	130	102	12
Folpet	18.6	1	259.9	130	14
Folpet	18.6	1	261.9	130	14
Chlorbenside	18.8	1	125	89	16
Chlorbenside	18.8	1	125	99	16
trans-chlordane	18.8	1	271.7	236.8	12
trans-chlordane	18.8	1	374.7	265.9	22
2,4 DDE	18.8	1	246	176.1	28
2,4 DDE	18.8	1	317.8	248	18
Paclobutrazol	18.8	1	125	89	16
Paclobutrazol	18.8	1	236	125	12
cis-chlordane	19	1	372.8	265.8	20
cis-chlordane	19	1	374.7	265.8	20
Pyrene	19	1	202.1	200	36
Pyrene	19	1	203.3	201	36

Name	RT	Window	Mass	Product mass	Collision energy
Endosulfan I	19	1	194.7	125	22
Endosulfan I	19	1	240.6	205.9	14
Flutriafol	19	1	123	75	24
Flutriafol	19	1	123	95	12
trans-Nonachlor	19	1	262.8	192.9	28
trans-Nonachlor	19	1	408.7	300	18
Fludioxonil	19.1	1	153.7	127	8
Fludioxonil	19.1	1	248	127	26
Chlorfenson (Ovex)	19.1	1	111	75	14
Chlorfenson (Ovex)	19.1	1	174.9	111	10
Tricyclazole	19.3	1	189	161	14
Tricyclazole	19.3	1	189	162	10
4,4-DDE	19.3	1	246	176.1	28
4,4-DDE	19.3	1	317.8	248	18
Myclobutanil	19.3	1	179	90	28
Myclobutanil	19.3	1	179	125	14
Bupirimate	19.3	1	208.1	165	12
Bupirimate	19.3	1	273.1	193.2	8
Flusilazole	19.3	1	233	151.9	14
Flusilazole	19.3	1	233	164.9	16
p-Terphenyl-d14 (SURR)	19.4	1	244	240.2	25
p-Terphenyl-d14 (SURR)	19.4	1	244	242.2	15
2,4 DDD	19.4	1	235	165.1	20
2,4 DDD	19.4	1	236.8	165	20
Dieldrin	19.4	1	262.8	190.9	30
Dieldrin	19.4	1	262.8	192.9	28
Chlorfenapyr	19.5	1	136.9	102	12
Chlorfenapyr	19.5	1	248.9	112	24
Ethylan (Perthane)	19.7	1	223.1	167	12
Ethylan (Perthane)	19.7	1	223.1	179	20
Endrin	19.8	1	245	173	22
Endrin	19.8	1	262.8	192.9	28
Endosulfan II	20	1	158.9	123	12
Endosulfan II	20	1	194.7	159	8
4,4 DDD	20	1	235	165.1	20
4,4 DDD	20	1	236.8	165	20
cis-Nonachlor	20.1	1	262.8	192.8	28
cis-Nonachlor	20.1	1	408.6	300	18
2,4'-DDT	20.1	1	235	165.1	20
2,4'-DDT	20.1	1	236.8	165	20
Endrin aldehyde	20.3	1	173	138.1	16
Endrin aldehyde	20.3	1	249.8	214.9	24
Famphur	20.4	1	217.9	79	24
Famphur	20.4	1	217.9	109	14
4,4'-Methoxychlor olefin	20.5	1	238.1	152.1	34
4,4'-Methoxychlor olefin	20.5	1	238.1	223.1	10
Benzyl butyl phthalate	20.7	1	149	65	20
Benzyl butyl phthalate	20.7	1	206.2	149	8

Table A2 (part 4). Selected reaction monitoring (SRM) transitions for data acquisition by GC-MS/MS.

Name	RT	Window	Mass	Product mass	Collision energy
Lenacil	20.7	1	153	82.1	16
Lenacil	20.7	1	153	110	14
Endosulfan sulfate	20.8	1	238.7	203.9	12
Endosulfan sulfate	20.8	1	271.7	236.8	12
4,4'-DDT	20.8	1	235	165.1	20
4,4'-DDT	20.8	1	236.8	165	20
Hexazinone	20.9	1	171.1	71.1	14
Hexazinone	20.9	1	171.1	85.1	12
2,4'-Methoxychlor	20.9	1	152	151.1	16
2,4'-Methoxychlor	20.9	1	227.1	121.1	10
Bis(2-ethylhexyl)adipate	21.1	1	129	55.1	14
Bis(2-ethylhexyl)adipate	21.1	1	129	101	6
Tebuconazole	21.1	1	125	89	16
Tebuconazole	21.1	1	250	125	20
Propargite	21.2	1	135.1	77.1	26
Propargite	21.2	1	135.1	107.1	12
Resmethrin	21.4	1	123.1	81.1	8
Resmethrin	21.4	1	143	128.1	10
Captafol	21.4	1	79	51	22
Captafol	21.4	1	79	77.1	12
Captafol	21.4	1	151.1	79.1	18
Iprodione	21.8	1	314	245	10
Iprodione	21.8	1	315.7	247	10
Endrin ketone	22	1	316.8	208.9	28
Endrin ketone	22	1	316.8	281	10
Bifenthrin	22	1	181	165.9	10
Bifenthrin	22	1	181	179	12
Tetramethrin	22.1	1	164	77.1	24
Tetramethrin	22.1	1	164	107.1	12
Benz[a]anthracene	22.2	1	225.9	224.1	34
Benz[a]anthracene	22.2	1	228	226	28
Chrysene-d12 (ISTD)	22.2	1	240.2	236.1	32
Chrysene-d12 (ISTD)	22.2	1	240.2	238.2	16
Chrysene	22.3	1	225.9	223.9	32
Chrysene	22.3	1	229.2	227.1	30
Phenothrin	22.8	1	123.1	79.1	14
Phenothrin	22.8	1	123.1	81.1	8
Bis(2-ethylhexyl)phthalate	22.9	1	149	65	22
Bis(2-ethylhexyl)phthalate	22.9	1	167.1	149	6
Tetradifon	23	1	159	111	20
Tetradifon	23	1	159	131	10
Pyriproxyfen	23.5	1	136.1	78	20
Pyriproxyfen	23.5	1	136.1	96	10
lambda-Cyhalothrin	23.9	1	180.9	152	22
lambda-Cyhalothrin	23.9	1	197.1	141.1	10
lambda-Cyhalothrin	23.9	1	207.9	180.9	8
Mirex	24	1	272	236.8	14
Mirex	24	1	273.8	238.8	14
Fenarimol	24.2	1	139	74.9	26
Fenarimol	24.2	1	139	111	14
Acrinathrin	24.2	1	208.1	180.9	8
Permethrine	25.2	1.6	183.1	153	12
Permethrine	25.2	1.6	183.1	168	12
Di-n-octyl phthalate	25.5	1	149	65	22
Di-n-octyl phthalate	25.5	1	149	93	16
Benzo[b]fluoranthene	26	1	126.1	113	12
Benzo[b]fluoranthene	26	1	252.1	250.1	32
Cyfluthrin	26	1.6	163	91.1	12
Cyfluthrin	26	1.6	163	127.1	6
Benzo[k]fluoranthene	26	1	250	248	32
Benzo[k]fluoranthene	26	1	252.1	250	34
Cypermethrin	26.4	1.6	163	91.1	12
Cypermethrin	26.4	1.6	163	127.1	6
Etofenprox	26.7	1	163.1	107.1	16
Etofenprox	26.7	1	163.1	135.1	10
Flucythrinate	26.7	1	157	107.1	12
Flucythrinate	26.7	1	199.1	157.1	8
Benzo[a]pyrene	26.7	1	250	248	36
Benzo[a]pyrene	26.7	1	252.1	250	34
Fluridone	26.9	1	328.1	189.1	38
Fluridone	26.9	1	329.1	328.5	12
Perylene-d12 (ISTD)	26.9	1	260.1	256.1	34
Perylene-d12 (ISTD)	26.9	1	264.2	260.1	36
Fenvalerate	27.3	1	125	89	18
Fenvalerate	27.3	1	167	125	10
Fluvalinate	27.4	1	180.8	152.1	22
Fluvalinate	27.4	1	250	55.1	16
Deltamethrin	28	1	181	152.1	22
Deltamethrin	28	1	252.8	92.9	16
Indeno[1,2,3-cd]pyrene	28.9	1	274	272	35
Indeno[1,2,3-cd]pyrene	28.9	1	276.1	274	40
Dibenz[a,h]anthracene	29	1	276	274	38
Dibenz[a,h]anthracene	29	1	278.1	276	34
Benzo[ghi]perylene	29.4	1	137.7	136.8	16
Benzo[ghi]perylene	29.4	1	276.1	274.1	38

Table A3 (part 1). Targeted analytes list with chromatographic retention time and calibration data for 1 µL injection method.

Compound name	Ret. time (min)	Cal. type	Number of points	RSD %	R^2	Calibration range (µg/L)
Phenol	6.8	Linear	11	1.68	0.9999	0.5–500
Aniline	6.85	Quadratic	9	1.69	0.9999	2.5–500
Bis(2-chloroethyl)ether	6.97	Linear	12	1.31	0.9999	0.1–500
2-Chlorophenol	7.04	Linear	12	4.15	0.9994	0.1–500
1,3-Dichlorobenzene	7.33	Linear	12	1.56	0.9999	0.1–500
1,4-Dichlorobenzene	7.47	Linear	12	1.30	0.9999	0.1–500
Benzyl alcohol	7.75	Linear	11	4.77	0.9992	0.5–500
1,2-Dichlorobenzene	7.76	Linear	12	1.28	0.9999	0.1–500
2-Methylphenol	7.97	Linear	12	2.49	0.9998	0.1–500
2,2'-Oxybis(1-chloropropane)	7.97	Linear	11	1.36	0.9999	0.5–500
N-Nitroso-di-n-propylamine	8.3	Linear	11	2.91	0.9997	0.5–500
3+4-Methylphenol	8.32	Linear	12	1.82	0.9999	0.2–1000
Hexachloroethane	8.44	Linear	12	1.83	0.9999	0.1–500
Nitrobenzene	8.59	Linear	12	5.32	0.9991	0.1–500
Isophorone	9.14	Linear	12	2.98	0.9997	0.1–500
2-Nitrophenol	9.3	Quadratic	11	1.52	0.9999	0.5–500
2,4-Dimethylphenol	9.47	Linear	12	2.09	0.9999	0.1–500
O,O,O-Triethyl thiophosphate	9.65	Linear	11	3.07	0.9996	0.05–50
Bis(2-chloroethoxy)methane	9.69	Linear	12	1.97	0.9999	0.1–500
2,4-Dichlorophenol	9.85	Quadratic	12	4.96	0.9993	0.1–500
1,2,4-Trichlorobenzene	10.02	Linear	12	1.11	0.9999	0.1–500
Naphthalene	10.17	Linear	12	1.75	0.9999	0.1–500
4-Chloroaniline	10.36	Linear	11	1.53	0.9999	0.5–500
Hexachlorobutadiene	10.51	Linear	12	1.41	0.9999	0.1–500
4-Chloro-3-methylphenol	11.54	Quadratic	11	2.66	0.9998	0.5–500
2-Methylnaphthalene	11.77	Linear	12	2.48	0.9998	0.1–500
1-Methylnaphthalene	11.97	Linear	12	2.60	0.9998	0.1–500
Hexachloro cyclopentadiene	12.13	Quadratic	12	1.68	0.9999	0.1–500
2,4,6-Trichlorophenol	12.42	Quadratic	11	4.73	0.9993	0.5–500
2,4,5-Trichlorophenol	12.48	Quadratic	11	6.26	0.9987	0.5–500
2-Chloronaphthalene	12.78	Linear	12	1.59	0.9999	0.1–500
2-Nitroaniline	13.04	Quadratic	11	1.93	0.9999	0.5–500
4-Nitrophenol	13.04	Quadratic	10	2.46	0.9998	1.5–500
1,4-Dinitrobenzene	13.34	Quadratic	11	3.08	0.9997	0.5–500
1,3-Dinitrobenzene	13.47	Quadratic	11	3.73	0.9996	0.5–500
Dimethyl phthalate	13.47	Linear	11	2.94	0.9997	0.5–500
Etridiazole	13.48	Linear	11	4.94	0.9991	0.05–50
2,6-Dinitrotoluene	13.54	Quadratic	11	2.59	0.9998	0.5–500
Acenaphthylene	13.59	Linear	12	2.17	0.9998	0.1–500
1,2-Dinitrobenzene	13.61	Quadratic	9	2.85	0.9997	2.5–500
3-Nitroaniline	13.84	Quadratic	10	3.44	0.9996	1.5–500
Acenaphthene	13.93	Linear	12	1.57	0.9999	0.1–500
Chloroneb	14.05	Linear	9	2.38	0.9997	0.25–50
2,4-Dinitrophenol	14.07	Linear	6	3.39	0.999	10–500
Pentachlorobenzene	14.19	Linear	11	1.78	0.9999	0.05–50
Dibenzofuran	14.27	Linear	11	3.61	0.9996	0.1–350
2,4-Dinitrotoluene	14.3	Quadratic	11	3.76	0.9996	0.5–500
2,3,5,6-Tetrachlorophenol	14.47	Quadratic	9	4.40	0.9993	2.5–500
2,3,4,6-Tetrachlorophenol	14.56	Quadratic	11	4.02	0.9995	0.5–500

Table A3 (part 2). Targeted analytes list with chromatographic retention time and calibration data for 1 µL injection method.

Compound name	Ret. time (min)	Cal. type	Number of points	RSD %	R^2	Calibration range (µg/L)
Diethyl Phthalate	14.81	Linear	10	3.76	0.9993	1.5–500
Fluorene	14.9	Linear	11	2.24	0.9998	0.1–350
Thionazin	14.94	Quadratic	10	3.80	0.9995	0.15–50
4-Chlorophenyl phenyl ether	14.95	Linear	12	2.67	0.9997	0.1–500
4-Nitroaniline	14.97	Quadratic	10	3.59	0.9996	1.5–500
4,6-Dinitro-2-methylphenol	15.1	Quadratic	4	12.69	0.9958	50–350
Diphenylamine	15.17	Linear	12	2.32	0.9998	0.1–500
Azobenzene	15.23	Linear	12	2.82	0.9997	0.1–500
Sulfotep	15.53	Quadratic	10	3.50	0.9996	0.15–50
Phorate	15.72	Quadratic	10	2.39	0.9998	0.15–50
4-Bromophenyl phenyl ether	15.81	Linear	12	2.50	0.9998	0.1–500
BHC, Alpha	15.81	Linear	11	3.05	0.9996	0.05–50
Hexachlorobenzene	15.87	Linear	12	1.98	0.9999	0.1–500
Pentachloroanisole	15.95	Linear	11	3.97	0.9994	0.05–50
Dimethoate	15.99	Quadratic	7	4.88	0.999	0.5–50
Atrazine	16.15	Quadratic	9	3.02	0.9997	0.25–50
BHC, Beta	16.18	Linear	11	2.33	0.9998	0.05–50
Pentachlorophenol	16.27	Quadratic	8	2.89	0.9997	3.5–500
BHC, Gamma	16.32	Linear	11	3.62	0.9995	0.05–50
Terbuthylazine	16.36	Quadratic	10	2.70	0.9997	0.15–50
Pyrimethanil	16.53	Quadratic	10	2.83	0.9997	0.15–50
Phenanthrene	16.57	Linear	12	2.50	0.9998	0.1–500
Terbacil	16.62	Quadratic	9	1.30	0.9999	0.25–50
Disulfoton	16.63	Quadratic	9	1.82	0.9999	0.25–50
Tefluthrine	16.64	Quadratic	11	3.11	0.9997	0.05–50
Anthracene	16.66	Linear	12	1.80	0.9999	0.1–500
BHC delta	16.73	Linear	11	4.35	0.9993	0.05–50
Carbazole	16.96	Linear	11	2.69	0.9997	0.5–500
Endosulfan ether	17.02	Linear	10	3.30	0.9995	0.15–50
Vinclozoline	17.2	Quadratic	10	1.96	0.9999	0.15–50
Methyl parathion	17.25	Quadratic	9	1.50	0.9999	0.25–50
Transfluthrin	17.27	Quadratic	10	2.03	0.9999	0.15–50
Heptachlor	17.4	Linear	11	6.27	0.9986	0.05–50
Di-n-butyl phthalate	17.66	Linear	10	5.88	0.9984	1.5–500
Pentachlorothioanisole	17.7	Linear	10	1.85	0.9999	0.15–50
Aldrin	17.92	Linear	10	2.56	0.9997	0.15–50
Parathion (ethyl parathion)	17.92	Quadratic	9	2.19	0.9998	0.25–50
Antraquinone	17.94	Quadratic	11	3.29	0.9997	0.05–50
Triadimefon	17.96	Quadratic	9	4.80	0.9992	0.25–50
4,4'-Dichlorobenzophenone	18.05	Quadratic	11	1.97	0.9999	0.05–50
Fenson	18.13	Linear	11	1.55	0.9999	0.05–50
MGK-264	18.15	Quadratic	10	3.85	0.9995	0.15–50
Cyprodinil	18.28	Quadratic	10	4.54	0.9993	0.15–50
Fipronil	18.29	Quadratic	7	2.68	0.9997	0.5–50
Isodrin	18.33	Linear	10	2.65	0.9997	0.15–50
Penconazole	18.37	Quadratic	10	5.24	0.9991	0.15–50
Bioallethrin	18.44	Quadratic	8	2.94	0.9997	0.35–50
Heptachlor epoxide	18.45	Quadratic	9	2.53	0.9997	0.25–50
Procymidone	18.55	Linear	11	4.12	0.9994	0.05–50

Table A3 (part 3). Targeted analytes list with chromatographic retention time and calibration data for 1 µL injection method.

Compound name	Ret. time (min)	Cal. type	Number of points	RSD %	R^2	Calibration range (µg/L)
Trifumizole	18.55	Quadratic	9	3.46	0.9996	0.25–50
Captan	18.55	Quadratic	6	5.56	0.9985	1–50
Fluoranthene	18.58	Linear	12	2.60	0.9998	0.1–500
Folpet	18.64	Quadratic	6	6.71	0.9978	1–50
Chlorbenside	18.76	Quadratic	11	5.08	0.9992	0.05–50
trans-chlordane	18.78	Linear	10	1.79	0.9999	0.15–50
2,4 DDE	18.79	Linear	11	3.60	0.9995	0.05–50
Paclobutrazol	18.84	Quadratic	9	2.47	0.9998	0.25–50
Pyrene	18.98	Linear	12	1.20	0.9999	0.1–500
cis-chlordane	18.98	Linear	10	4.70	0.999	0.15–50
Endosulfan I	18.99	Linear	8	3.94	0.9991	0.35–50
Flutriafol	19.01	Quadratic	9	3.66	0.9995	0.25–50
trans-Nonachlor	19.02	Linear	8	2.38	0.9997	0.35–50
Fludioxonil	19.08	Quadratic	10	3.99	0.9995	0.15–50
Chlorfenson (Ovex)	19.11	Linear	11	3.15	0.9996	0.05–50
Tricyclazole	19.24	Quadratic	6	6.52	0.9978	1–50
4,4-DDE	19.29	Linear	11	2.52	0.9998	0.05–50
Myclobutanil	19.32	Quadratic	10	3.36	0.9996	0.15–50
Bupirimate	19.34	Quadratic	8	4.38	0.9993	0.35–50
Flusilazole	19.35	Quadratic	9	5.20	0.9991	0.25–50
2,4 DDD	19.4	Linear	11	3.78	0.9995	0.05–50
Dieldrin	19.42	Linear	8	1.65	0.9998	0.35–50
Chlorfenapyr	19.5	Quadratic	6	1.84	0.9998	1–50
Ethylan (Perthane)	19.7	Quadratic	11	4.16	0.9995	0.05–50
Endrin	19.8	Linear	8	5.01	0.9987	0.35–50
Endosulfan II	19.98	Linear	8	7.16	0.9974	0.35–50
4,4 DDD	20.03	Quadratic	11	5.21	0.9992	0.05–50
cis-Nonachlor	20.07	Linear	7	4.82	0.9986	0.5–50
2,4'-DDT	20.09	Quadratic	11	3.45	0.9996	0.05–50
Endrin aldehyde	20.27	Linear	7	5.54	0.9979	0.5–50
Famphur	20.44	Quadratic	9	3.16	0.9997	0.25–50
4,4'-Methoxychlor olefin	20.52	Quadratic	10	3.78	0.9995	0.15–50
Benzyl butyl phthalate	20.66	Quadratic	10	4.50	0.9993	1.5–500
Lenacil	20.69	Quadratic	8	3.71	0.9995	0.35–50
Endosulfan sulfate	20.77	Quadratic	8	4.66	0.9991	0.35–50
4,4'-DDT	20.83	Quadratic	11	2.33	0.9998	0.05–50
Hexazinone	20.9	Quadratic	10	4.87	0.9993	0.15–50
2,4'-Methoxychlor	20.94	Quadratic	9	2.02	0.9999	0.25–50
Bis(2-ethylhexyl)adipate	21.06	Quadratic	10	4.34	0.9994	1.5–500
Tebuconazole	21.15	Quadratic	9	4.93	0.9991	0.25–50
Propargite	21.15	Quadratic	8	2.98	0.9996	0.35–50
Resmethrin	21.36	Quadratic	9	1.82	0.9999	0.25–50
Captafol	21.37	Quadratic	5	8.22	0.9969	5–50
Iprodione	21.77	Linear	5	7.28	0.9963	1–35
Endrin ketone	21.97	Quadratic	6	2.41	0.9997	1–50
Bifenthrin	22.03	Quadratic	9	1.34	0.9999	0.25–50
Tetramethrin	22.11	Quadratic	9	4.85	0.9993	0.25–50
Benz[a]anthracene	22.18	Linear	12	7.50	0.9982	0.1–500
Chrysene	22.31	Linear	12	1.12	0.9999	0.1–500

Table A3 (part 4). Targeted analytes list with chromatographic retention time and calibration data for 1 µL injection method.

Compound name	Ret. time (min)	Cal. type	Number of points	RSD %	R^2	Calibration range (µg/L)
Phenothrin isomer 1	22.83	Quadratic	7	2.29	0.9997	0.5–50
Bis(2-ethylhexyl)phthalate	22.94	Quadratic	10	4.33	0.9994	1.5–500
Tetradifon	22.97	Quadratic	10	2.51	0.9998	0.15–50
Phenothrin isomer 2	23.05	Quadratic	9	1.12	0.9999	0.25–50
Pyriproxyfen	23.53	Quadratic	10	1.17	0.9999	0.15–50
lambda-Cyhalothrin	23.88	Quadratic	10	5.98	0.9989	0.15–50
Mirex	24.02	Quadratic	11	1.87	0.9999	0.05–50
Fenarimol	24.17	Quadratic	10	2.58	0.9998	0.15–50
Acrinathrin	24.23	Linear	5	7.97	0.9957	1–35
Permethrine	25.17	Quadratic	10	3.08	0.9997	0.15–50
Di-n-octyl phthalate	25.5	Quadratic	11	2.93	0.9998	0.5–500
Benzo[b]fluoranthene	25.98	Linear	11	2.62	0.9998	0.1–350
Cyfluthrin	26.04	Linear	8	6.63	0.9981	0.25–35
Benzo[k]fluoranthene	26.06	Linear	11	6.91	0.9985	0.1–350
Cypermethrin	26.43	Linear	8	6.22	0.9983	0.25–35
Flucythrinate isomer 1	26.52	Linear	8	9.90	0.9959	0.25–35
Etofenprox	26.69	Quadratic	11	4.41	0.9994	0.05–50
Benzo[a]pyrene	26.74	Linear	12	6.97	0.9983	0.1–500
Flucythrinate isomer 2	26.74	Linear	8	10.31	0.9956	0.25–35
Fluridone	26.88	Quadratic	6	5.05	0.9988	1–50
Fenvalerate isomer 1	27.3	Linear	8	9.09	0.9965	0.25–35
Fenvalerate isomer 2	27.5	Quadratic	8	1.81	0.9999	0.35–50
Fluvalinate	27.5	Linear	6	7.99	0.9962	0.5–35
Deltamethrin	28.02	Linear	8	9.57	0.9959	0.25–35
Indeno[1,2,3-cd]pyrene	28.92	Linear	12	3.32	0.9996	0.1–500
Dibenz[a,h]anthracene	29	Linear	12	6.19	0.9986	0.1–500
Benzo[ghi]perylene	29.4	Linear	11	5.47	0.9991	0.1–350

Table A4 (part 1). Repeatability test over six repeated injections for the first three calibration levels.

Level 1 (0.1 µg/L EPA Mix)	Area RSD%	Level 2 (0.5 µg/L EPA Mix) (0.05 µg/L pesticides)	Area RSD%	Level 3 (1.5 µg/L EPA Mix) (0.15 µg/L Pesticides)	Area RSD%
Bis(2-chloroethyl)ether	7.6	Phenol	8.3	4-Nitrophenol	13.5
2-Chlorophenol	12.4	Benzyl alcohol	13.2	3-Nitroaniline	4.6
1,3-Dichlorobenzene	7.1	2,2'-Oxybis(1-chloropropane)	8.8	Diethyl Phthalate*	1.8
1,4-Dichlorobenzene	10.5	N-Nitroso-di-n-propylamine	9.6	Thionazin	7.5
1,2-Dichlorobenzene	7.3	2-Nitrophenol	15.6	4-Nitroaniline	11.7
2-Methylphenol	11.8	O,O,O-Triethyl thiophosphate	10.3	Sulfotep	6.6
3+4-Methylphenol	7.5	4-Chloroaniline	8.5	Phorate	13.6
Hexachloroethane	7.7	4-Chloro-3-methylphenol	8.2	Terbuthylazine	14.7
Nitrobenzene	13.3	2,4,6-Trichlorophenol	16.9	Pyrimethanil	13.3
Isophorone	11.6	2,4,5-Trichlorophenol	4.2	Endosulfan ether	7.6
2,4-Dimethylphenol	12.5	2-Nitroaniline	9.4	Vinclozoline	14.1
Bis(2-chloroethoxy)methane	9.2	1,4-Dinitrobenzene	15.3	Transfluthrin	10.1
2,4-Dichlorophenol	10.6	Dimethyl phthalate	3.7	Di-n-butyl phthalate*	6.7
1,2,4-Trichlorobenzene	7.1	1,3-Dinitrobenzene	13.7	Pentachlorothioanisole	11.6
Naphthalene	11.3	Etridiazole	12.1	Aldrin	10.9
Hexachlorobutadiene	8.8	2,6-Dinitrotoluene	7.9	MGK-264	14.6
2-Methylnaphthalene	11.8	Pentachlorobenzene	5.3	Cyprodinil	8.5
1-Methylnaphthalene	9.1	2,4-Dinitrotoluene	12.9	Isodrin	7.5

*Matrix area correction applied

Table A4 (part 2). Repeatability test over six repeated injections for the first three calibration levels.

Level 1 (0.1 µg/L EPA Mix)	Area RSD%	Level 2 (0.5 µg/L EPA Mix) (0.05 µg/L pesticides)	Area RSD%	Level 3 (1.5 µg/L EPA Mix) (0.15 µg/L Pesticides)	Area RSD%
Hexachlorocyclopentadiene	11.3	2,3,4,6-Tetrachlorophenol	15.2	Penconazole	10.8
2-Chloronaphthalene	9.5	BHC, Alpha	11.5	*trans*-chlordane	13.3
Acenaphthylene	8.3	Pentachloroanisole	12.4	*cis*-chlordane	17.2
Acenaphthene	12.2	BHC, Beta	11.1	Fludioxonil	14.0
Dibenzofuran	11.2	BHC, Gamma	12.1	Myclobutanil	16.4
Fluorene	10.1	Tefluthrine	6.7	4,4'-Methoxychlor olefin	7.6
4-Chlorophenyl phenyl ether	14.3	BHC delta	13.8	Benzyl butyl phthalate*	7.8
Diphenylamine	13.6	Carbazole	4.1	Hexazinone	12.2
Azobenzene	15.1	Heptachlor	9.7	Bis(2-ethylhexyl)adipate	9.3
4-Bromophenyl phenyl ether	14.5	Antraquinone	7.2	Bis(2-ethylhexyl)phthalate*	6.3
Hexachlorobenzene	9.5	4,4'-Dichlorobenzophenone	5.8	Tetradifon	13.3
Phenanthrene	12.1	Fenson	11.3	Pyriproxyfen	10.8
Anthracene	10.7	Procymidone	9.3	lambda-Cyhalothrin	10.3
Fluoranthene	10.4	Chlorbenside	16.6	Fenarimol	7.3
Pyrene	11.5	2,4 DDE	8.5	Permethrine	7.4
Benz[a]anthracene	12.6	Chlorfenson (Ovex)	10.3		
Chrysene	10.8	4,4-DDE	9.6		
Benzo[b]fluoranthene	12.7	2,4 DDD	5.4		
Benzo[k]fluoranthene	7.8	Ethylan (Perthane)	11.8		
Benzo[a]pyrene	13.3	4,4 DDD	12.1		
Indeno[1,2,3-cd]pyrene	14.1	2,4'-DDT	11.6		
Dibenz[a,h]anthracene	13.3	4,4'-DDT	7.4		
Benzo[ghi]perylene	10.9	Mirex	15.5		
		Di-n-octyl phthalate	11.8		
		Etofenprox	8.5		

*Matrix area correction applied

Table A5 (part 1). External calibration results over the six lower concentration levels for 10 µL injection volume. Calibration type: Linear with Offset.

Compound name	Ret. time (min)	RSD %	R^2	Calibration range (µg/L)
Phenol	6.82	5.827	0.9974	0.1–5
Bis(2-chloroethyl)ether	6.99	6.158	0.9973	0.1–5
2-Chlorophenol	7.06	5.137	0.9981	0.1–5
1,3-Dichlorobenzene	7.35	6.924	0.9965	0.1–5
1,4-Dichlorobenzene	7.49	6.225	0.9972	0.1–5
Benzyl alcohol	7.73	7.491	0.9955	0.1–5
1,2-Dichlorobenzene	7.77	6.655	0.9968	0.1–5
2-Methylphenol	7.96	5.548	0.9979	0.1–5
2,2'-Oxybis(1-chloropropane)	7.96	4.933	0.9984	0.1–5
N-Nitroso-di-n-propylamine	8.28	8.069	0.9957	0.1–5
3+4-Methylphenol	8.3	5.4	0.998	0.2–10
Hexachloroethane	8.44	6.624	0.9969	0.1–5
Nitrobenzene	8.58	7.095	0.9965	0.1–5
Isophorone	9.12	8.64	0.995	0.1–5
2-Nitrophenol	9.27	7.858	0.9959	0.1–5
2,4-Dimethylphenol	9.45	6.26	0.9973	0.1–5
O,O,O-Triethyl thiophosphate	9.63	5.822	0.9979	0.01–0.5
Bis(2-chloroethoxy)methane	9.67	4.971	0.9983	0.1–5

Compound name	Ret. time (min)	RSD %	R^2	Calibration range (µg/L)
2,4-Dichlorophenol	9.82	6.455	0.9971	0.1–5
1,2,4-Trichlorobenzene	10	4.92	0.9983	0.1–5
Naphthalene	10.15	5.484	0.9979	0.1–5
4-Chloroaniline	10.33	7.46	0.9962	0.1–5
Hexachlorobutadiene	10.5	7.562	0.9961	0.1–5
4-Chloro-3-methylphenol	11.52	5.559	0.9979	0.1–5
2-Methylnaphthalene	11.76	5.238	0.9981	0.1–5
1-Methylnaphthalene	11.96	5.229	0.9981	0.1–5
Hexachlorocyclopentadiene	12.12	8.436	0.9953	0.1–5
2,4,6-Trichlorophenol	12.39	6.765	0.9969	0.1–5
2,4,5-Trichlorophenol	12.45	4.841	0.9984	0.1–5
2-Chloronaphthalene	12.77	4.476	0.9986	0.1–5
2-Nitroaniline	13.01	6.349	0.9973	0.1–5
4-Nitrophenol	13.02	5.285	0.9982	0.1–5
1,4-Dinitrobenzene	13.32	7.349	0.9966	0.1–5
1,3-Dinitrobenzene	13.46	9.303	0.9946	0.1–5
Etridiazole	13.47	10.701	0.9926	0.01–0.5
2,6-Dinitrotoluene	13.53	8.853	0.9951	0.1–5

Table A5 (part 2). External calibration results over the six lower concentration levels for 10 µL injection volume. Calibration type: Linear with Offset.

Compound name	Ret. time (min)	RSD %	R^2	Calibration range (µg/L)
Acenaphthylene	13.58	5.857	0.9977	0.1–5
3-Nitroaniline	13.83	6.355	0.9975	0.1–5
Acenaphthene	13.93	4.809	0.9984	0.1–5
Pentachlorobenzene	14.18	3.135	0.9993	0.01–0.5
Dibenzofuran	14.26	2.829	0.9994	0.1–5
2,4-Dinitrotoluene	14.28	8.078	0.996	0.1–5
2,3,4,6-Tetrachlorophenol	14.51	5.157	0.9982	0.1–5
Fluorene	14.89	3.348	0.9992	0.1–5
Thionazin	14.94	6.962	0.9967	0.01–0.5
4-Nitroaniline	14.94	7.142	0.9968	0.1–5
4-Chlorophenyl phenyl ether	14.94	2.354	0.9996	0.1–5
Diphenylamine	15.16	3.381	0.9992	0.1–5
Azobenzene	15.22	4.729	0.9985	0.1–5
Sulfotep	15.52	5.906	0.9975	0.01–0.5
BHC, Alpha	15.8	4.226	0.9987	0.01–0.5
4-Bromophenyl phenyl ether	15.8	2.648	0.9995	0.1–5
Hexachlorobenzene	15.86	2.622	0.9995	0.11–5.5
Pentachloroanisole	15.94	2.26	0.9996	0.01–0.5
BHC, Beta	16.17	2.297	0.9996	0.01–0.5
Pentachlorophenol	16.23	3.460	0.9990	0.1–5
BHC, Gamma	16.31	1.899	0.9997	0.01–0.5
Terbuthylazine	16.35	5.053	0.9982	0.01–0.5
Pyrimethanil	16.52	3.248	0.9993	0.01–0.5
Phenanthrene	16.56	1.987	0.9997	0.1–5
Tefluthrine	16.63	4.291	0.9987	0.01–0.5
Anthracene	16.65	2.519	0.9996	0.1–5
BHC delta	16.72	4.018	0.9988	0.01–0.5
Carbazole	16.95	3.903	0.9989	0.1–5
Endosulfan ether	17.01	3.983	0.9989	0.01–0.5
Vinclozoline	17.19	8.106	0.9953	0.01–0.5
Transfluthrin	17.26	2.156	0.9997	0.01–0.5
Heptachlor	17.39	5.421	0.9979	0.01–0.5
Pentachlorothioanisole	17.69	3.715	0.999	0.01–0.5
Aldrin	17.91	1.185	0.9999	0.01–0.5
Antraquinone	17.92	6.349	0.9972	0.01–0.5
4,4'-Dichlorobenzophenone	18.04	3.075	0.9993	0.01–0.5

Compound name	Ret. time (min)	RSD %	R^2	Calibration range (µg/L)
Fenson	18.11	2.643	0.9995	0.01–0.5
MGK-264	18.14	4.468	0.9986	0.01–0.5
Cyprodinil	18.28	5.557	0.9979	0.01–0.5
Isodrin	18.32	3.196	0.9993	0.01–0.5
Penconazole	18.34	4.005	0.9989	0.01–0.5
Fluoranthene	18.56	3.524	0.9991	0.1–5
Chlorbenside	18.75	4.649	0.9986	0.01–0.5
trans-chlordane	18.77	1.881	0.9997	0.01–0.5
2,4 DDE	18.77	2.25	0.9996	0.01–0.5
cis-chlordane	18.97	4.502	0.9985	0.01–0.5
Pyrene	18.97	3.172	0.9993	0.1–5
Fludioxonil	19.06	5.077	0.9983	0.01–0.5
Chlorfenson (Ovex)	19.09	2.688	0.9995	0.01–0.5
4,4-DDE	19.27	3.746	0.999	0.01–0.5
Myclobutanil	19.3	6.293	0.9974	0.01–0.5
2,4 DDD	19.38	3.654	0.9991	0.01–0.5
Ethylan (Perthane)	19.68	4.178	0.9988	0.01–0.5
4,4 DDD	20.01	3.725	0.999	0.01–0.5
2,4'-DDT	20.07	5.827	0.9977	0.01–0.5
4,4'-Methoxychlor olefin	20.5	4.098	0.9988	0.01–0.5
4,4'-DDT	20.81	6.096	0.9975	0.01–0.5
Hexazinone	20.87	7.15	0.9967	0.01–0.5
Benz[a]anthracene	22.16	6.761	0.9971	0.1–5
Chrysene	22.28	2.88	0.9994	0.1–5
Tetradifon	22.94	6.388	0.9973	0.01–0.5
Pyriproxyfen	23.51	7.741	0.9961	0.01–0.5
lambda-Cyhalothrin	23.85	7.276	0.9965	0.01–0.5
Mirex	23.99	4.533	0.9985	0.01–0.5
Fenarimol	24.15	5.538	0.998	0.01–0.5
Permethrine	25.15	7.274	0.9964	0.01–0.5
Benzo[b]fluoranthene	25.97	6.034	0.9977	0.1–5
Benzo[k]fluoranthene	26.04	4.895	0.9985	0.1–5
Etofenprox	26.67	5.84	0.9977	0.01–0.5
Benzo[a]pyrene	26.73	7.993	0.9962	0.1–5
Indeno[1,2,3-cd]pyrene	28.9	7.545	0.9965	0.1–5
Dibenz[a,h]anthracene	28.97	7.735	0.9963	0.1–5
Benzo[ghi]perylene	29.38	5.294	0.9982	0.1–5

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