Poster Reprint

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Automated Sample Preparation and Analysis of OCPs in Drinking Water

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Introduction

The Analysis of Organochlorine Pesticides (OCP's) in drinking water is generally performed by manual liquid-liquid extraction with a concentration step performed before analysis by triple quadrupole GC/MS.

Traditionally, volumes as high as 500 and 1000 mL are used and at least 100 to 200 mL of water sample is required with often over 25 mL of extraction solvent needed to extract. Hence, an additional concentration step via evaporation becomes needed.

Benefits of Automation

Sample preparation automation provides multiple benefits:

- Less room for human error – can be left unattended to run 24/7 if desired.
  For this method, the user only needs to add salt and sample (15 mL) to the headspace vial – the rest of the process is fully automated.
- Higher reproducibility as the sample prep robot will perform actions consistently for each sample.
- Significantly less sample and solvents are used resulting in a more sustainable approach.
- Lower costs and higher throughput.

Sample Extraction Steps

ISTD Spiking

- Using a dedicated (for ISTD) liquid tool with a 10 µL syringe, 2 µL of ISTD (from a 2 mL autosampler vial) were pipetted into 20 mL headspace (HS) vials containing sample/standards.

Solvent Addition

- 2 mL of 90:10 isooctane:ethyl acetate solvent was added to the sample vial (20 mL HS)

Extraction

- The vial was then transported to the vortex mixer and then vortexed at 2,000 rpm for 60 seconds

Sample Injection

- Using a dedicated (for sample extracts) liquid tool with a 10 µL syringe, 1 µL of analyte protectants and then 8 µL of sample extract were injected onto the **8890/7010 Series GC/TQ**

Maximized Robustness

The solution utilizes **midcolumn backflush** which minimizes heavy matrix contamination on the head of the column and to the MS source whilst not impacting mass spec performance as constant flow is maintained throughout the flow path.

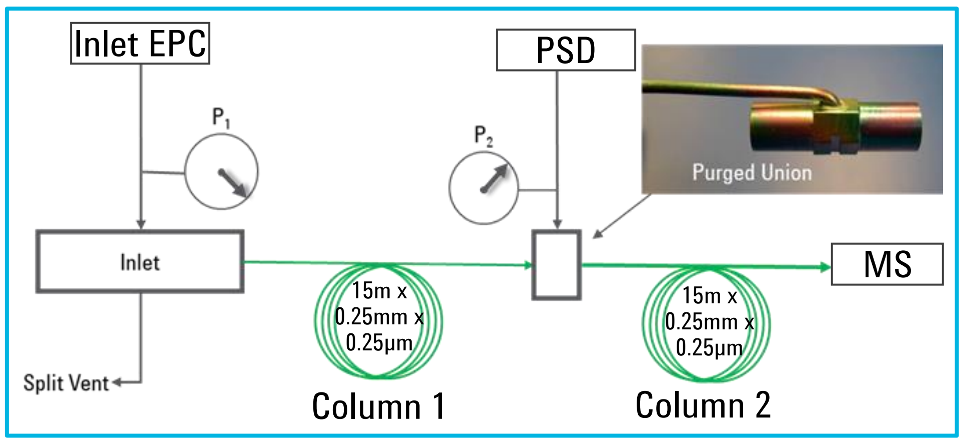


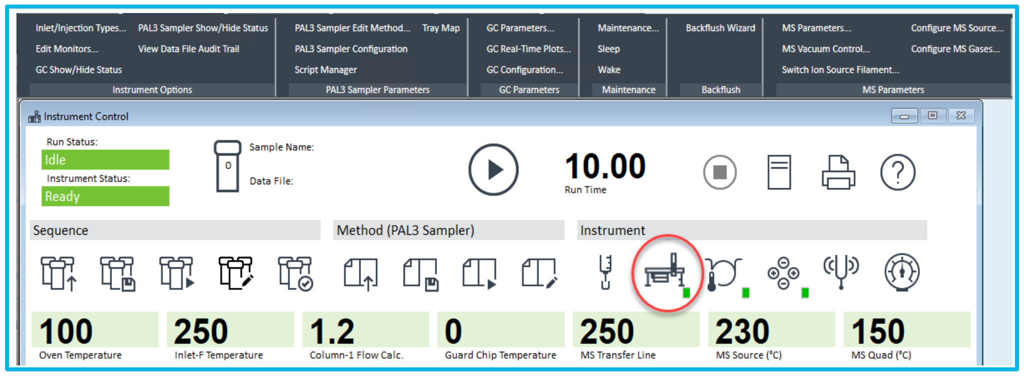
Figure 1. Midcolumn backflush configuration compromising of two GC columns connected with the purged ultimate union (PUU) with the pneumatic switching device (PSD) module supplying pressure.

The solution additionally is supplied with **JetClean** technology that provides cleaning of the MS electron ionization (EI) source in situ.

This is implemented as a 2 minute 'clean' method that is run every 2 weeks and maintains the MS ion source in a steady state.

As a results, no manual cleaning had been needed in over 6 months of routine operation.

PAL3 Control in MassHunter 13

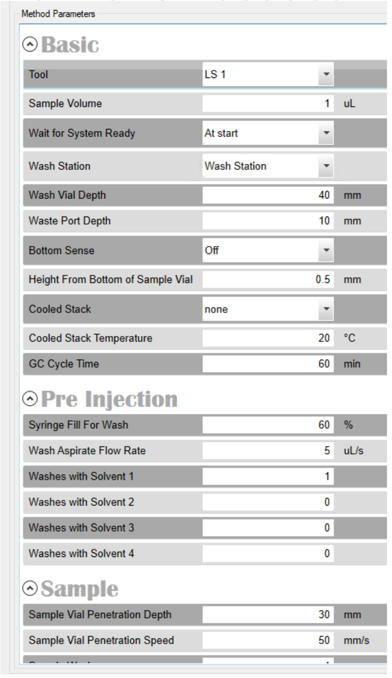


Run Status: Idle
Instrument Status: Ready
Sample Name:
Data File:
0
10.00 Run Time
100 Oven Temperature
250 Inlet-F Temperature
1.2 Column-1 Flow Calc.
0 Guard Chip Temperature
250 MS Transfer Line
230 MS Source (°C)
150 MS Quad (°C)

Figure 2. MassHunter Acquisition 13 with embedded PAL3 support.

Full run control from MassHunter Acquisition 13 with no additional software required making sequence generation and run control seamless (Fig. 2).

Sample prep steps and acquisition are combined into a single method by importing the PAL script into MassHunter.


Method Parameters

Basic

Tool	LS 1	
Sample Volume	1	uL
Wait for System Ready	At start	
Wash Station	Wash Station	
Wash Vial Depth	40	mm
Waste Port Depth	10	mm
Bottom Sense	Off	
Height From Bottom of Sample Vial	0.5	mm
Cooled Stack	none	
Cooled Stack Temperature	20	°C
GC Cycle Time	60	min

Pre Injection

Syringe Fill For Wash	60	%
Wash Aspirate Flow Rate	5	uL/s
Washes with Solvent 1	1	
Washes with Solvent 2	0	
Washes with Solvent 3	0	
Washes with Solvent 4	0	

Sample

Sample Vial Penetration Depth	30	mm
Sample Vial Penetration Speed	50	mm/s

Results and Discussion

Excellent Calibration Performance and Repeatability

Full UKAS Accreditation achieved in record time. Table 1 demonstrates the data collected over 6 sequences.

- Excellent linearity over **0.01 – 0.250 µg/L** ($R^2 > 0.997$)
- Low RSDs at low and mid-level (< 10%, most analytes < 5%).

High Sensitivity at 0.01 µg/L (ppb)

- Low **LOQs ≤ 0.01 µg/L (ppb)** were achieved for all targets
- High sensitivity was achieved at the lowest tested level (lowest S/N=49 for dieldrin).

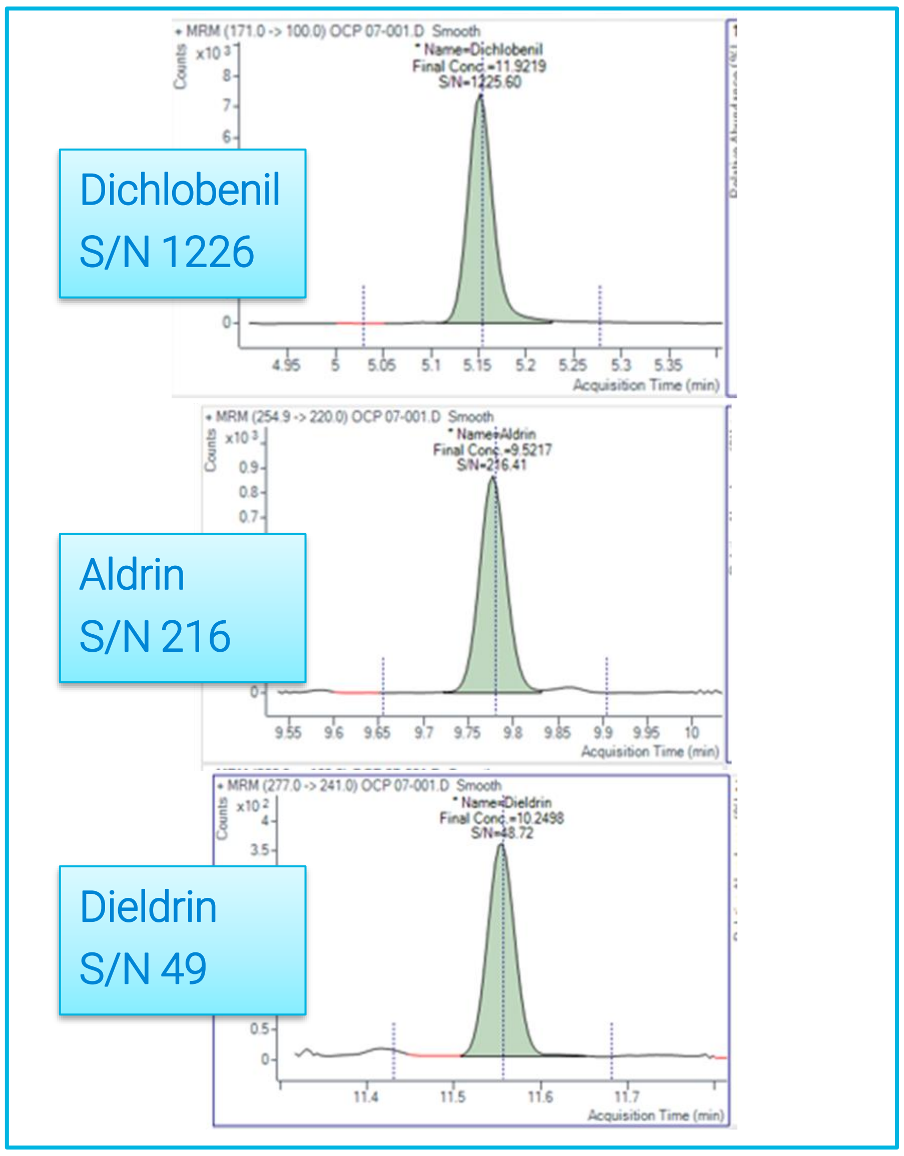


Figure 3. Quantifier MRM response at 0.01 µg/L.

Analyte	Average Curve Fit R^2	RSD % at 0.02 µg/L	RSD % at 0.18 µg/L	LOQ µg/L
Aldrin	0.9991	7.7	7	0.007
Chlorpropham	0.9985	4.5	2.6	0.004
Chlorpyrifos	0.9992	4.9	4.2	0.006
Chlorthal Dimethyl	0.9996	4.5	1.9	0.005
Diazinon	0.9991	5.2	3	0.007
Dichlobenil	0.9996	3.6	4.2	0.004
Dieldrin	0.9992	4.5	2.5	0.006
Ethoprop	0.9989	5.4	3.3	0.006
Heptachlor	0.9995	5.7	4.6	0.009
Heptachlor Epoxide A	0.9993	5.4	3.2	0.005
Heptachlor Epoxide B	0.9975	4.9	6.1	0.005
Lindane	0.9994	5.1	8	0.01
Propachlor	0.9991	4.5	3	0.005
Propetamphos	0.9981	4.3	2.8	0.005
Propham	0.999	3.4	2.7	0.004
Propyzamide	0.9988	3.9	1.7	0.005
Tecnazene	0.9991	5.6	3.1	0.008
Triallate	0.9991	6.1	3	0.005
Trifluralin	0.9987	4.5	3.1	0.006

Table 1. Calibration performance, stability, and LOQs for 19 POPs.

Analyte Protectants for Increased Ruggedness

Analyte protectants were added via reversed sandwich injection mode to each sample. Analyte protectants coat the active sites across the GC flow path and allow for consistent response in various matrices and across the calibration range.

Solvent Vent Injection Mode for Increased Sensitivity

The multimode inlet (MMI) operated in solvent vent mode allows for large volume injections due to controlled evaporation of the sample solvent. The solvent is effectively “blown down” inside the inlet resulting in high sensitivity, even for thermally labile and active compounds.

Key PAL 3 RTC Modules Utilized

Liquid Handling

Dedicated tool for each liquid handling step eliminates potential for cross-contamination.

Smart syringes are automatically recognized and configured by the PAL using RFID chips

- User will be alerted if the wrong syringe is installed
- EMF counters ensure consumables are replaced

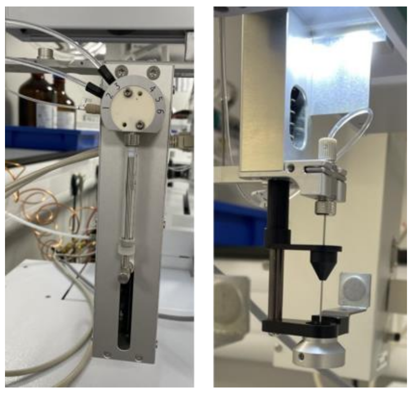
Fast Wash Station

Considerably reduces carry-over from sample to sample, Syringe needle is immersed during cleaning.

Tubing attaches to independent large volume (2.5 L) solvent bottles – very infrequent refilling of wash solvent

Waste port tubing runs to a large solvent waste container – reduces need to empty waste

Diluter Dispenser



Eliminates need for pre-mixing of solvents – method can be configured to add multiple solvents in the correct ratio.

Vortex Mixer

Mixing up to 2000 rpm resulting in complete extraction in minimal time

Only one sample is vortexed at a time – PAL prepares the next sample during the current run

The sample is ready to inject as soon as the instrument returns to ready state.

Key Learnings

- On-rail vortexing capability required to achieve full automation
- Incorporating concurrent midcolumn backflush has resulted in the GC column and MS source needing minimal maintenance
- The only column that needs any maintenance is the first column that can be changed without the need to vent or even cool the mass spectrometer
- PTFE tipped syringes were found necessary for injection consistency.

Conclusions

- Excellent sensitivity for OCP's (< 0.01 ug/L) was achieved with only 15ml of water taken.
- The extraction has been shown to be reproducible and robust requiring limited analyst supervision.
- The automation is embedded within MassHunter requiring no additional software for the control and sequencing of the analysis.
- The incorporation of mid-column backflush has resulted in consistent responses and retention times throughout the sequences and has minimized contamination of the MS source. The additional JetClean option has resulted in no manual source cleaning being required to date.
- The automation has been configured to enable minimal analyst interaction by the incorporation of a diluter/dispenser into a large 2.5 L solvent bottle. This way non-mixed solvents can be used together with a fast wash station that means that no contamination will result from waste solvents.

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