

Determination of Organophosphorus Pesticides by Automated Solid Phase Extraction (SPE) - Initial Demonstration of Capability for Selected Compounds

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Introduction

Organophosphorus (OP) compounds are the most widely used pesticides in the world. They are readily hydrolysed and therefore do not persist in the environment for very long nor accumulate in the body fat of humans or other animals. The ubiquitous nature of the OP pesticides result in routine exposure for humans through the consumption of fresh and processed vegetables, contact with pesticide-contaminated surfaces, breathing air near pesticide applications, and drinking pesticide contaminated water. The OP pesticides interfere with the nervous system of both insects and humans. In humans, these compounds block the production of cholinesterase. The main target organs in humans are the nervous system, respiratory tract, and cardiovascular system. The EPA classifies most OP compounds as toxicity class I (highly toxic) or toxicity class II (moderately toxic).

EPA Methods 1657A and 3535A detail the procedures for the determination of Organophosphorus compounds in aqueous samples. The OP compounds are extracted using solid phase extraction (SPE) based on the procedure outlined in Method 3535A for OP compounds by Method 8141. The analysis is performed with capillary GC using a FPD (flame photometric detector). This short note presents data from the City of Fort Worth, TX for the initial demonstration of capability using the Horizon Technology automated SPE-DEX[®] 4790 Extractor System. Automated SPE provides the benefits of high sample throughput, low solvent consumption, safe working conditions and consistent, reliable data.

Instrumentation

- SPE-DEX[®] 4790 Extractor System (Horizon Technology, Salem, NH).
- SPE Disk: Empore[™] 3M C18, 47 mm
- Gas chromatography Conditions:
6890 FPD/FPD

Inlet A	on	225°C
Inlet B	off	
Detector A	on	250°C
Detector B	on	250°C
Auxiliary	off	

Oven Program:

	Initial Temp.	80°C	
	Initial Time:	0.00 min.	
Level	(°C/min.)	Final Temp. °C	Final Time (min.)
1	20.0	170	0.00
2(A)	10.0	280	5.53
3(B)	0.0	0	0.00
Total run time = 21.03 min.			

Inlet Constant Pressure 25.0 Psi

Gas: He

Detector Gases: He, Hydrogen, and Air

Column type 1: DB-5MS 30m x 0.32 mm ID

Film thickness 0.50 um

Column type 2: DB-1701 30 m x 0.32 mm ID

Film thickness 0.25 um

Columns 1 & 2 connected to a press-fit "Y"-shaped splitter

Method Summary

- 1) IPR samples: Four replicates prepared using 500 mL of DI water at pH 5.0 – 9.0, spiked at 5.00 µg/L.
- 2) MDL samples: Seven replicates prepared using 500 mL of DI water at pH 5.0 – 9.0 and spiked at 1.25 µg/L for each compound.
- 3) SPE-DEX[™] 4790 Extractors are purged in preparation for extraction.
- 4) The 47 mm, Empore[™] C18 disks are placed in the Disk Holder Assemblies and loaded onto the Extractors.
- 5) Sample bottles are loaded onto the Extractor Bottle Holders and the collection vessels attached to the Extractors.
- 6) IPR and MDL samples are extracted using Horizon Technology's SPE-DEX[™] 4790 Automated Extractor System.
- 7) At the end of the extraction run, the extracts are dried using sodium sulfate and concentrated with LABCONCO Rapid Vap System.
- 8) Dried and concentrated extracts analysed using capillary GC – 6890 dual FPD detector.

Results

Hexane was used as the extraction solvent to eliminate the solvent exchange step. Data using methylene chloride as an extraction solvent showed comparable results (not presented in this paper).

The Initial Precision and Recovery (IPR) data for the selected OP compounds are shown in Tables 2 and 3. The Method Detection Limits (MDL) are shown in Tables 4 and 5. The % RSD for the IPR data for all compounds fall below 4 % with recoveries between 61.0 and 120 %. The MDL for each compound was calculated by multiplying the STD DEV from the replicate study by the student t value of 3.143.

Conclusions

The City of Fort Worth, TX uses Method 1657A for permit work. Acceptable recovery limits and MDL values for the compounds are specified in Method 1657A Section 9.2. Results presented in this paper from an independent laboratory indicate that automated SPE using Horizon Technology's SPE-DEX™ 4790 Extractors provide accurate and precise results for the determination of Organophosphorus Compounds in aqueous samples. Benefits of Automated SPE include reduced solvent usage, elimination of emulsions, reduced exposure to solvents, improved recoveries and consistency of results, increased productivity, and reduction in labour costs.

Table 1: Extraction Method 8141

Step	Solvent	Soak Time	Dry Time
Prewet 1	Acetone	1:00 min	1:30 min
Prewet 2	MeOH	1:00 min	0 sec
Prewet 3	Reagent water	1:00 min	0 sec
Process Sample			
Air Dry			3:00 min
Rinse 1	Acetone	1:00 min	1:00 min
Rinse 2	Hexane	1:00 min	1:00 min
Rinse 3	Hexane	1:30 min	2:00 min
Rinse 4	Hexane	1:30 min	2:00 min

Table 2. Initial Precision & Recovery (IPR) – Column 1

Compounds	IPR 1	IPR 2	IPR 3	IPR 4	Mean	Mean % Recovery	STD DEV	RSD
Spike Level	5.00 µg/L							
Demeton-O & S	3.65	3.55	3.53	3.47	3.55	71.0	0.075	2.11
Diazinon	4.04	4.04	4.08	3.97	4.03	80.7	0.046	1.13
Disulfoton	3.06	3.06	3.04	3.03	3.05	61.0	0.015	0.49
Chlorpyrifos	3.99	4.00	4.07	3.96	4.01	80.1	0.047	1.16
Parathion, methyl	4.25	4.28	4.36	4.25	4.29	85.7	0.052	1.21
Malathion	4.33	4.33	4.44	4.30	4.35	87.0	0.062	1.42
Parathion, ethyl	4.11	4.10	4.21	4.14	4.14	82.8	0.050	1.20
Ethion	4.01	4.06	4.07	4.02	4.04	80.8	0.029	0.73
EPN	4.08	4.16	4.10	4.06	4.10	82.0	0.043	1.05
Azinphos-methyl	5.68	6.13	6.00	6.19	6.00	120.0	0.228	3.79

Table 3. Initial Precision & Recovery (IPR) – Column 2

Compounds	IPR 1	IPR 2	IPR 3	IPR 4	Mean	Mean % Recovery	STD DEV	RSD
Spike Level	5.00 µg/L							
Demeton-O & S	3.12	3.07	3.09	2.95	3.06	61.2	0.075	2.44
Diazinon	4.08	4.09	4.19	4.04	4.10	82.0	0.064	1.56
Disulfoton	3.04	3.04	3.11	3.00	3.05	61.0	0.046	1.50
Chlorpyrifos	3.95	4.01	4.07	3.98	4.00	80.1	0.051	1.28
Parathion, methyl	3.94	3.91	4.04	3.92	3.95	79.1	0.060	1.51
Malathion	4.09	4.09	4.18	4.13	4.12	82.5	0.043	1.04
Parathion, ethyl	4.06	4.11	4.21	4.14	4.13	82.6	0.063	1.52
Ethion	4.00	4.03	4.09	4.03	4.04	80.8	0.038	0.93
EPN	4.16	4.12	4.18	4.15	4.15	83.1	0.025	0.60
Azinphos-methyl	4.32	4.21	4.27	4.26	4.27	85.3	0.045	1.06

Table 4. Method Detection Limits (MDL) – Column 1

Compounds	MDL 1	MDL 2	MDL 3	MDL 4	MDL 5	MDL 6	MDL 7	Mean	STD DEV	MDL
Spike Level	1.25 µg/L									
Demeton-O & S	0.88	0.89	0.90	0.87	0.90	0.89	0.91	0.891	0.013	0.042
Diazinon	0.95	0.96	0.96	0.96	0.98	0.94	0.94	0.956	0.014	0.044
Disulfoton	0.54	0.55	0.55	0.54	0.56	0.54	0.53	0.544	0.010	0.031
Chlorpyrifos	0.96	0.97	0.97	0.98	0.99	0.96	0.96	0.970	0.012	0.036
Parathion, methyl	1.02	1.08	1.07	1.08	1.10	1.05	1.06	1.066	0.026	0.081
Malathion	1.11	1.12	1.11	1.12	1.14	1.09	1.10	1.113	0.016	0.050
Parathion, ethyl	1.04	1.05	1.04	1.03	1.09	0.99	1.00	1.034	0.033	0.104
Ethion	1.01	1.01	1.03	1.04	1.06	0.98	1.01	1.020	0.026	0.081
EPN	1.12	1.14	1.14	1.12	1.18	1.12	1.12	1.134	0.022	0.070
Azinphos-methyl	1.82	1.84	1.87	1.85	1.97	1.92	1.88	1.879	0.051	0.162

Table 5. Method Detection Limits (MDL) – Column 2

Compounds	MDL 1	MDL 2	MDL 3	MDL 4	MDL 5	MDL 6	MDL 7	Mean	STD DEV	MDL
Spike Level	1.25 µg/L									
Demeton-O & S	0.56	0.55	0.55	0.55	0.54	0.51	0.57	0.547	0.019	0.059
Diazinon	1.00	1.00	0.99	1.02	1.01	0.99	1.01	1.003	0.011	0.035
Disulfoton	0.54	0.54	0.54	0.55	0.57	0.54	0.53	0.544	0.013	0.040
Chlorpyrifos	0.98	0.99	0.98	1.00	1.00	0.96	0.97	0.983	0.015	0.047
Parathion, methyl	0.98	0.98	0.98	1.01	1.03	0.95	0.98	0.987	0.026	0.081
Malathion	1.02	1.02	1.03	1.05	1.04	1.02	1.01	1.027	0.014	0.043
Parathion, ethyl	0.96	0.95	0.97	0.97	0.99	0.96	0.95	0.964	0.014	0.044
Ethion	1.04	1.03	1.04	1.05	1.08	1.02	1.03	1.041	0.020	0.061
EPN	1.17	1.14	1.15	1.14	1.18	1.12	1.14	1.149	0.020	0.064
Azinphos-methyl	1.29	1.21	1.17	1.23	1.31	1.18	1.21	1.229	0.053	0.167