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Application Note

Analysis of organochlorine pesticides and PCBs using EPA method 608.3

Organochlorine pesticides are widely used and occur in a variety of sample matrices including water, soil, and food. These toxic pesticide residues persist in the environment. They are usually present in samples at a very low concentration and there can be many potentially interfering compounds extracted from the matrix during sample preparation *(1)*. Polychlorinated biphenyls, PCBs, were once widely used in transformer oils because of their desirable chemical and physical properties. They also persist in the environment and are considered toxic *(2)*. For both of these compound classes, a sensitive, selective method is required.

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Determination of Organochloride pesticides and PCBs

USEPA Method 608.3 is a gas chromatography (GC) method for the determination of organochloride pesticides and PCB's in industrial discharges and other environmental samples by GC combined with a halogen-specific detector (HSD) *(3)*. Many environmental samples have significant matrix interferences, yet a very low reporting level is needed requiring an extremely sensitive and selective detector

Methods 608, 608.1 and 608.2 have been available for many years as guidance to meet requirements for low concentration of analytes in environmental samples. These methods specifically cited the use of the electron capture detector (ECD). In 2016, Method 608.3 replaced these methods from 1993. Method 608.3 includes options for halogen-specific detectors other than ECD, such as the XSD, by OI Analytical. Instrument method information and QC for the XSD are presented, and sample results from two labs using ECD and XSD detectors, will be compared.

Instrumentation and methodology

Table 1. Instrument parameters

5370 XSD detector	5370
Base	300 ˚C
Reactor	1100 ˚C
Air flow (measured)	25 mL/min
Air flow (set on GC)*	210 mL/min
Detector	300 ˚C
Vent valve ON	2.4 minutes
Vent valve OFF	5.0 minutes
Gas chromatograph	**Agilent 7890A**
Column	Restek Rtx – CL Pesticides
Dimensions	30 meter, 0.32 mm ID, 0.32 µm
Inlet temperature	250 ˚C
Inlet liner	Restek Topaz 4 mm precision with wool
Column flow	0.8 mL/min constant flow
Split ratio	2
Oven program	Hold at 100 ˚C for 1 minute 40 ˚C/minute to 200 ˚C 10 ˚C/minute to 320 ˚C Hold 2 minutes

***** Flow must be set high because of restrictors located in the vent valve manifold

The instrumentation used for this study was an Agilent 7890A Gas Chromatograph with an OI Analytical 5370 Halogen Selective Detector (XSD) equipped with the venting option. The venting option vents the solvent off before it reaches the detector. The detector consists of a ceramic probe with a platinum coil and bead inserted into a high-temperature reactor. The elevated temperature of the reactor causes alkali metal atoms to be released from the ceramic probe and deposited on the bead. The GC column effluent is combusted in a stream of air and passed over the bead. The halogenated compounds in the effluent react with the alkali metal atoms on the bead surface resulting in an increase in thermal electron emission. This emission is collected and the measured current is proportional to the mass of halogen in the sample. High halogen selectivity vs. hydrocarbon (Cl: HC > 10^4) simplifies analyses and minimizes or eliminates sample dilution.

Target compounds can deteriorate in the inlet so before running the instrument, daily inlet maintenance must be performed including replacing the inlet liner. A standard containing Endrin and 4,4'-DDT is then analyzed to check for breakdown. The % breakdown for both compounds must be less than 20% before proceeding. Separate, multi-point calibrations were run for organochloride pesticides, PCBs, Toxaphene, and Chlordane in Hexane. The Agilent GC ChemStation OpenLab data system was used to generate calibration curves using linear weighted calibration.

Method detection limit (MDL) studies at levels below the reporting level were conducted over a 3-day period. Initial demonstrations of capability were run using mid-level standards. Real world samples and associated QC were run. Several standards with 10-100 ppm sulfur and a standard with 50 ppm phthalate were analyzed on the XSD to see if there was any interference or quenching effect. See **Table 1** for instrument parameters.

Calibration

Calibration criteria for linear regression was better than the required 0.920 with most compounds having a correlation coefficient of >0.995 and average response factor relative standard deviation of <20%. Please see **Table 2** for QC results.

Table 2. Calibration

Compound	Analyte	Cal range (PPB)	Avg RF	% RSD	% RSE (Avg RF calc.)	Correlation coefficient	% RSE (Linear 1/C Cal.)	MDL (PPB)	IDOC precision (% RPD)	IDOC accuracy (% Rec)
1	TCMX (SS)	5-2000	0.889	5.12	4.47	0.999	4.78	1.12	1.18	107.6
2	alpha-BHC	5-2000	1.128	7.79	6.89	0.999	7.36	0.92	1.91	111.0
3	gamma-BHC	5-2000	1.054	12.02	10.93	0.998	11.68	0.90	1.18	115.7
4	beta-BHC	5-2000	1.176	7.50	6.70	0.999	7.16	0.96	1.28	108.2
5	delta-BHC	5-2000	1.123	7.77	6.94	0.999	7.41	0.91	1.19	110.8
6	Heptachlor	5-2000	0.975	6.01	5.30	0.999	5.67	0.94	1.13	110.8
7	Aldrin	5-2000	0.895	11.40	10.09	0.999	10.78	0.98	1.20	114.5
8	Heptachlor epoxide	5-2000	1.014	9.70	8.65	0.999	9.25	1.01	1.22	113.8
9	gamma-Chlordane	5-2000	1.113	9.30	8.38	0.999	8.96	1.04	1.02	112.4
10	alpha-Chlordane	5-2000	1.035	11.30	11.20	0.997	11.97	1.50	1.10	119.3
11	4,4'-DDE	5-2000	0.763	8.21	7.46	0.999	7.98	0.73	1.20	114.0
12	Endosulfan I	5-2000	0.852	9.11	8.21	0.999	8.78	0.97	1.33	115.4
13	Dieldrin	5-2000	0.886	10.03	9.04	0.999	9.66	0.92	1.14	114.0
14	Endrin	5-2000	0.618	8.20	7.34	0.999	7.85	1.30	1.96	126.3
15	4,4'-DDD	5-2000	0.828	6.26	5.56	0.999	5.94	1.05	1.05	103.1
16	Endosulfan II	5-2000	0.804	10.78	9.77	0.999	10.45	1.18	2.00	115.1
17	4,4'-DDT	5-2000	0.720	4.47	3.96	0.999	4.24	1.01	1.27	109.8
18	Endrin aldehyde	5-2000	0.920	11.13	10.06	0.999	10.75	1.14	1.47	113.0
19	Methoxychlor	5-2000	0.417	3.24	2.80	0.999	3.00	1.11	1.24	110.9
20	Endosulfan sulfate	5-2000	0.836	9.78	8.85	0.999	9.46	0.91	1.18	114.4
21	Endrin ketone	5-2000	0.908	9.94	9.03	0.999	9.66	0.98	1.30	112.9
22	Decachlorobiphenyl (SS)	5-2000	1.086	8.44	7.49	0.999	8.01	0.98	1.09	115.2
23	Arochlor 1016	25-2000	0.509	5.60	6.15	0.999	6.64	3.48	1.15	95.6
24	Arochlor 1260	25-2000	0.750	12.3	17.5	0.995	18.9	5.56	0.89	101.5
25	Chlordane	50-5000	0.489	14.6	14.6	0.997	14.6	9.94	9.61	102.4
26	Toxaphene	200-10000	1.650	5.75	5.24	0.998	5.74	133	0.64	94.6

Sample Analysis

Samples were extracted at Test America and split with OI Analytical for analysis. Test America screened samples to determine what dilution to use. Samples with compounds over the calibration levels were diluted so the detector would not be saturated. In general, results between the two labs were very close. Please see **Table 3** for sample results. Instrument results are reported as well as the final concentration using the dilution factors. Subsequently, the XSD detector was tested for resistance to interference from sulfur and phthalates, which are well known to cause high levels of interference on ECD systems. The sulfur and phthalate standards added at 50 ppm did not cause interferences in low ppb pesticide standard.

Table 3. Results

Surrogate true concentration is 20 ppb. Matrix spike true concentration is 50 ppb and 2000 ppb for Toxaphene. *Surrogate is diluted out.

Table Results (ppb)

		157		157MS		163		165		166		167		168		169	
		ECD	XSD	ECD	XSD	ECD	XSD	ECD	XSD	ECD	XSD	ECD	XSD	ECD	XSD	ECD	XSD
		1x	1x	1x	1x	1x	1x	20x	20x	4x	4x	1x	1x	1x	1x	1x	1x
1	TCMX(SS)	10.6	16.9	12	16.4	13.6	18.4	*	*	8.4(2.1)	13.9(3.48)	12.4	16	12.4	17.6	12.1	16.8
2	alpha BHC	<5	<5	35.8	42.5	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	< 5
3	gamma BHC	<5	<5	35.4	45.0	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
4	beta BHC	<5	<5	35.0	42.6	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
5	delta BHC	<5	<5	34.7	42.6	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
6	Heptachlor	<5	<5	36.1	45.0	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
7	Aldrin	<5	<5	32.6	45.1	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
8	Heptachlor epoxide	<5	<5	32.8	42.5	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
9	gamma chlordane	<5	<5	33.3	43.3	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
10	alpha chlordane	<5	<5	32.4	46.7	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
11	44 DDE	<5	<5	34.2	44.1	<5	<5	1640 (81.9)	1340 (66.9)	33.6 (8.4)	30.2 (7.54)	<5	<5	<5	<5	<5	<5
12	Endosulfan 1	<5	<5	31.7	42.3	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
13	Dieldrin	<5	<5	32.2	44.2	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
14	Endrin	<5	<5	33.9	55.7	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
15	44 DDD	<5	<5	33.5	41.9	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
16	Endosulfan II	<5	<5	29.9	42.2	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
17	44 DDT	<5	<5	40.8	43.5	<5	<5	1210 (60.7)	1020 (51)	53.2 (13.3)	57.2 (14.3)	<5	<5	<5	<5	<5	<5
18	Endrin Aldehylde	<5	<5	26.6	38.0	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
19	Methoxychlor	<5	<5	41.3	45.6	<5	<5	120 (6)	<100	<20	<20	<5	<5	<5	<5	<5	<5
20	Endosulfan Sulfate	<5	<5	33.4	43.5	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
21	Endrin Ketone	<5	<5	33.1	42.6	<5	<5	<100	<100	<20	<20	<5	<5	<5	<5	<5	<5
22	DCB (SS)	11.7	17.2	10.6	16.5	13.3	18.4	*	*	*	*	11.4	16	11.4	17.4	11.1	16.8
23	Arochlor 1016	<25	<25	<25	<25	<25	<25	<500	<500	<100	<100	<25	<25	<25	<25	<25	<25
24	Arochlor 1260	<25	<25	<25	<25	<25	<25	<500	<500	<100	<100	<25	<25	<25	<25	<25	<25
25	Chlordane	<50	<50	<50	<50	<50	<50	<1000	<1000	<200	<200	<50	<50	<50	<50	<50	<50
26	Toxaphene	<200	<200	1040	720	<200	<200	2680 (134)	3640 (182)	400 (100)	440 (110)	<200	<200	<200	<200	<200	<200

Surrogate true concentration is 20 ppb. Matrix spike true concentration is 50 ppb and 2000 ppb for Toxaphene. *Surrogate is diluted out.

Table Results (ppb)

		170		171		172		173		174	
		ECD	XSD	ECD	XSD	ECD	XSD	ECD	XSD	ECD	XSD
		40x	40x	20x	20x	40x	40x	20x	20x	1x	1x
1	TCMX(SS)	*	*	*	*	*	*	*	*	13.2	18.7
2	alpha BHC	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
3	gamma BHC	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
4	beta BHC	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
5	delta BHC	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
6	Heptachlor	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
7	Aldrin	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
8	Heptachlor epoxide	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
9	gamma chlordane	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
10	alpha chlordane	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
11	44 DDE	1920 (48)	1970 (49.3)	752 (37.6)	662 (33.1)	1080 (27.1)	1020 (25.4)	668 (33.3)	554 (27.7)	<5	<5
12	Endosulfan 1	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
13	Dieldrin	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
14	Endrin	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
15	44 DDD	396 (9.9)	<200	<100	<100	<200	<200	<100	<100	<5	<5
16	Endosulfan II	264 (6.6)	<200	<100	<100	<200	<200	<100	<100	<5	<5
17	44 DDT	4480 (112)	4340 (108.5)	846 (42.3)	828 (41.4)	2860 (71.5)	2840 (71)	1630 (81.5)	1390 (69.3)	<5	<5
18	Endrin Aldehylde	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
19	Methoxychlor	456 (11.4)	<200	<100	<100	372 (9.3)	<200	<100	<100	<5	<5
20	Endosulfan Sulfate	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
21	Endrin Ketone	<200	<200	<100	<100	<200	<200	<100	<100	<5	<5
22	DCB (SS)	*	*	*	*	*	*	*	*	12.1	18.7
23	Arochlor 1016	<1000	<1000	<500	<500	<1000	<1000	<25	<25	<25	<25
24	Arochlor 1260	<1000	<1000	<500	<500	<1000	<1000	<25	<25	<25	<25
25	Chlordane	<2000	<2000	<1000	<1000	<2000	<2000	<50	<50	<50	<50
26	Toxaphene	8320 (208)	14030 (351)	<4000	<4000	6000 (150)	7800 (195)	<200	<200	<200	<200

Figure 2. 200 ppb pesticide standard

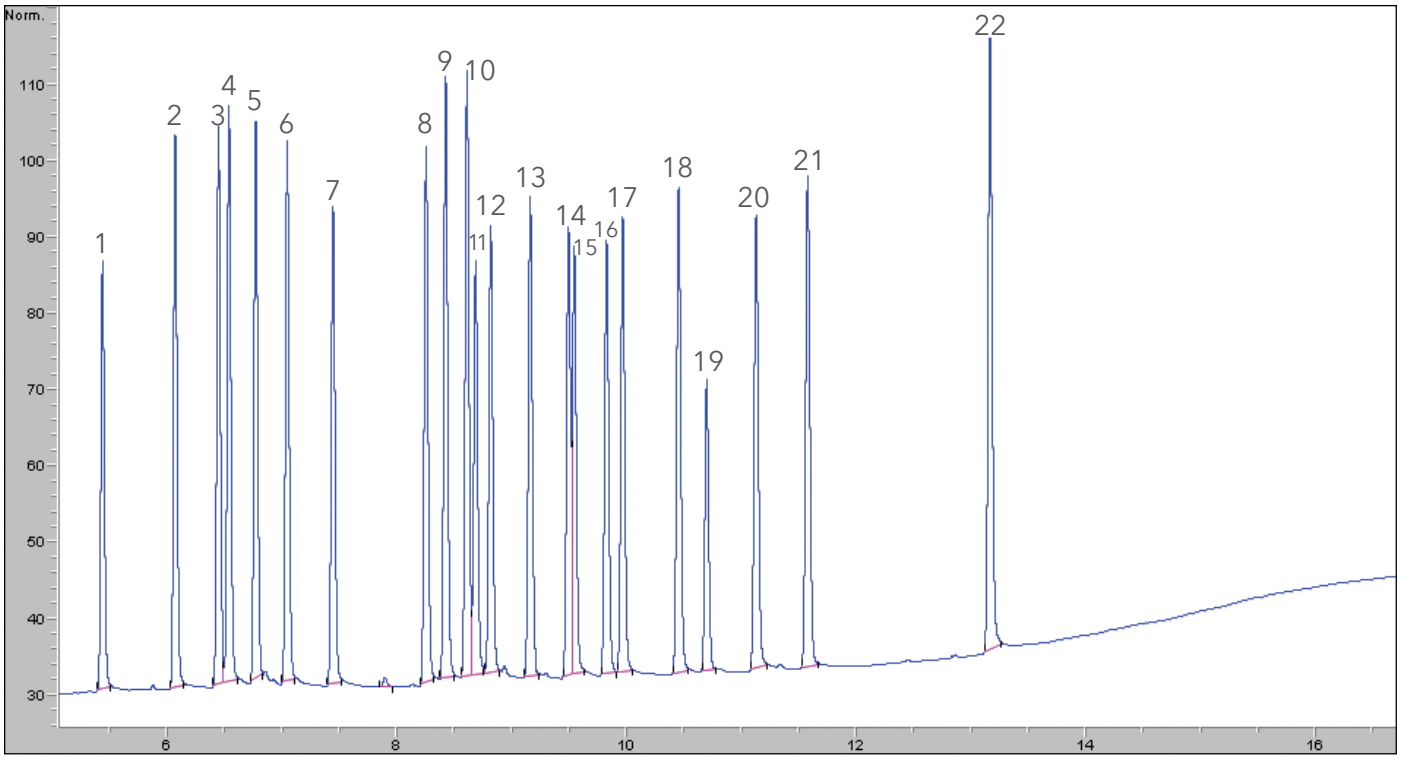


Figure 3. 500 ppb Arochlor 1016 and 1260 standard

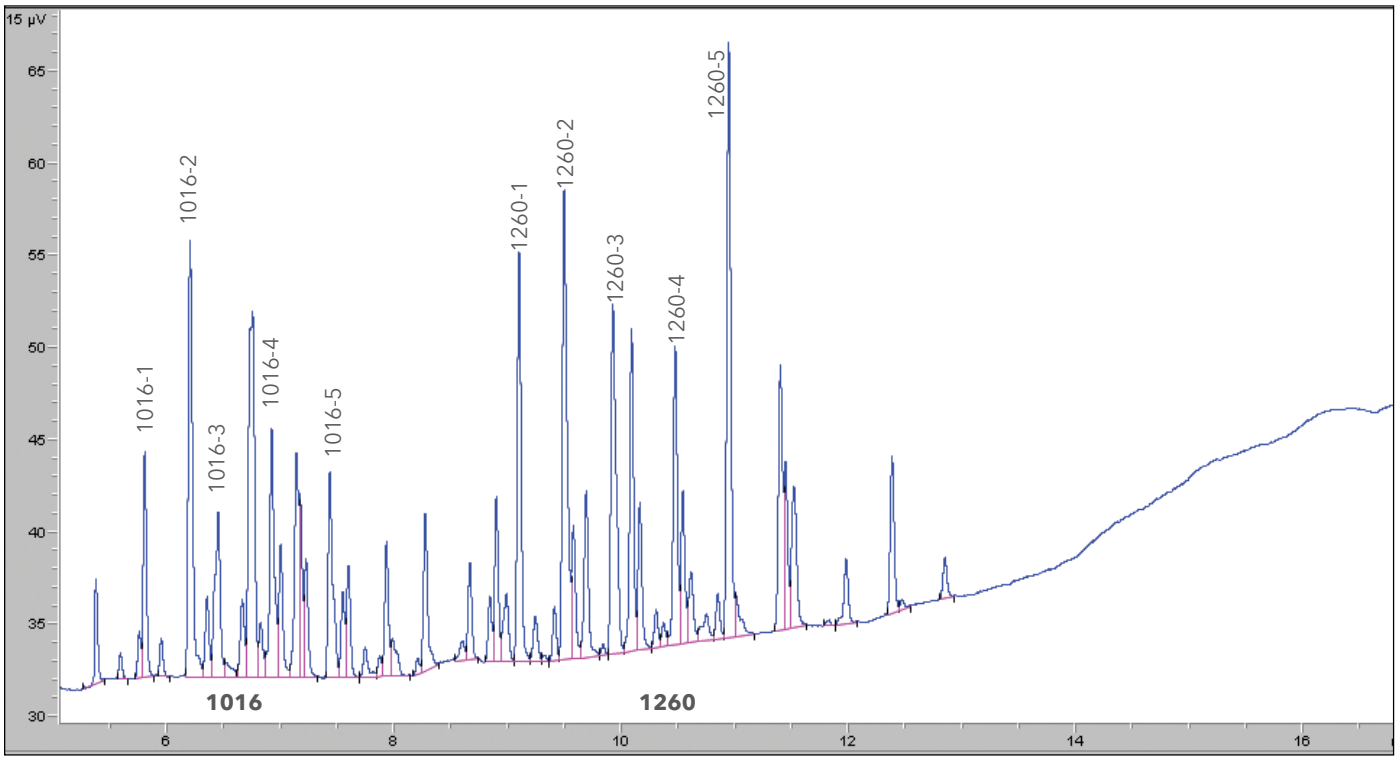


Figure 4. 500 ppb Chlordane standard

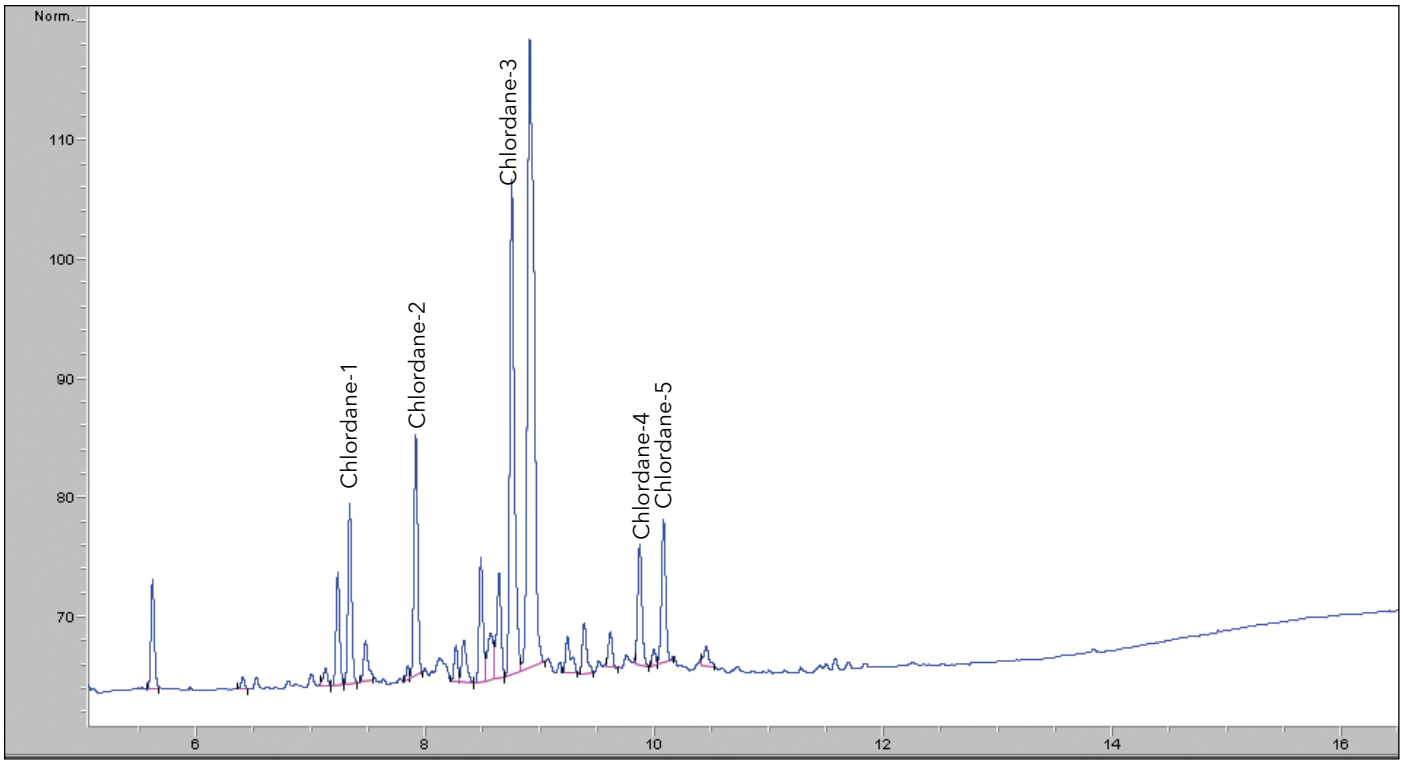


Figure 5. 2000 ppb Toxaphene standard

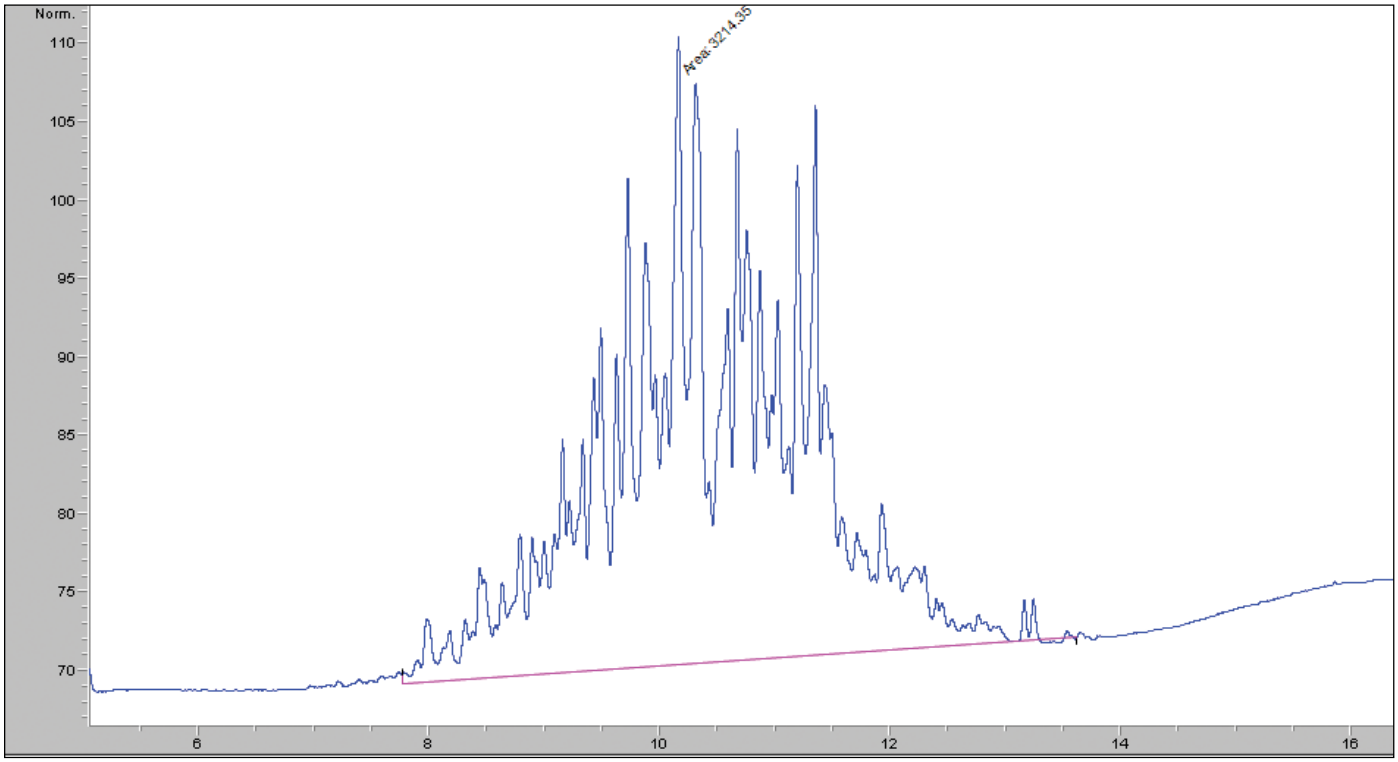


Figure 6. Sample -165 at 20x on ECD

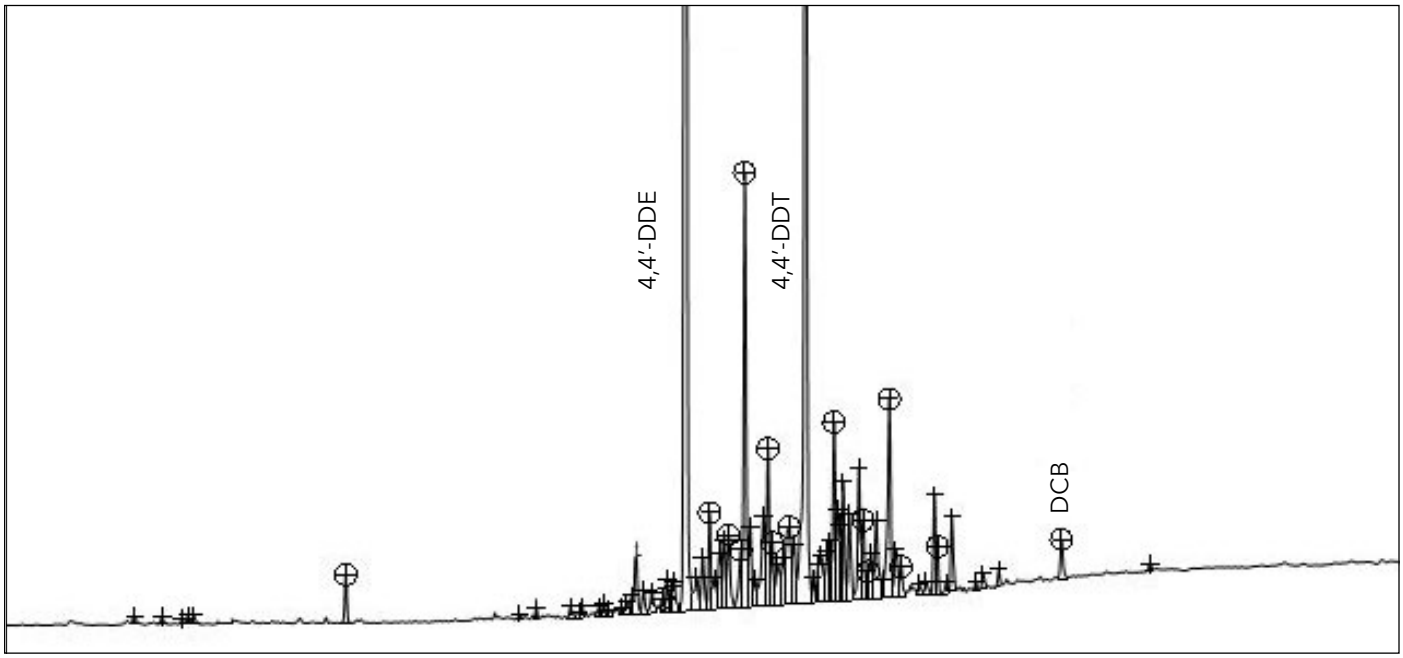
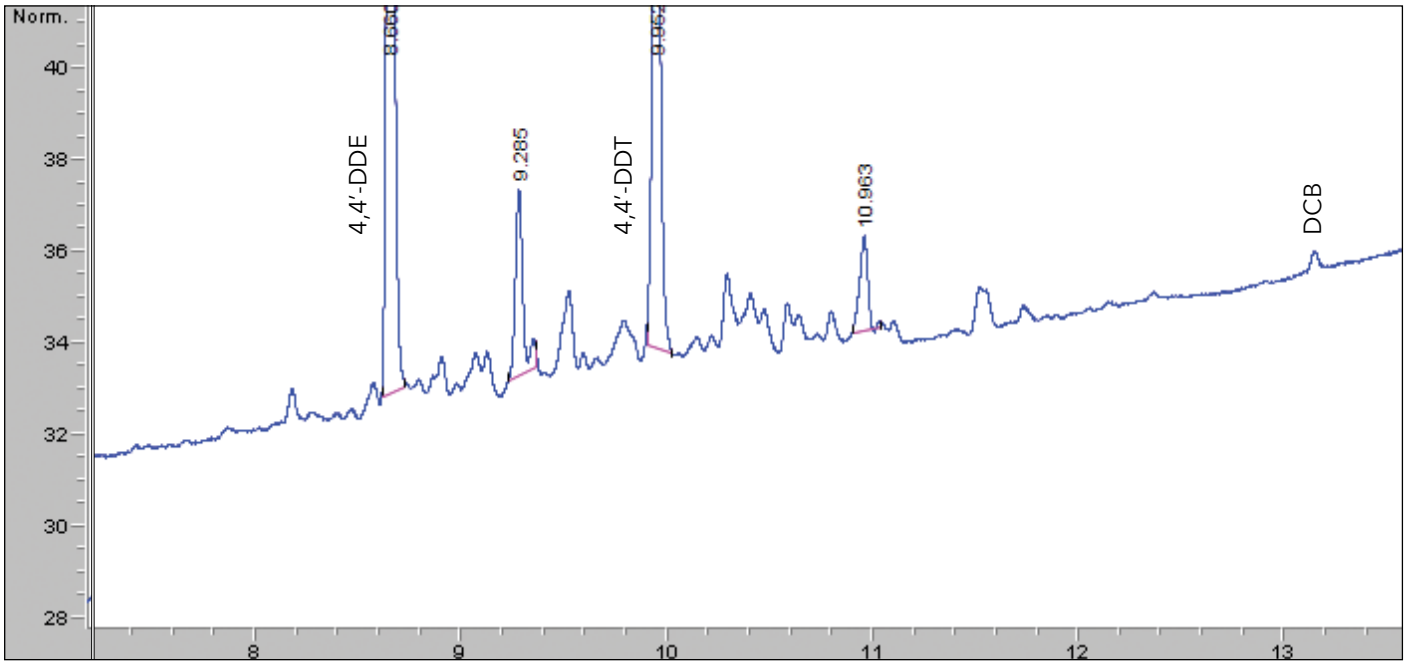


Figure 7. Sample -165 at 20x on XSD



Conclusions

Detection limits, sample results and quality control were comparable to the ECD method demonstrating that the XSD is a viable alternative to ECD for method 608.3. The 5370 XSD is also more resistant to interferences from hydrocarbons, phthalates and sulfur, and does not have a radioactive source.

References

1. OI Analytical. Multi-element Analysis of Pesticides Using GC Systems Equipped with Multiple Selective GC Detectors. 1999.
2. USEPA, Method 608.3: Organochlorine Pesticides and PCBs by GC/HSD. 2016

Acknowledgements

Thank you to Restek for providing analytical columns for this study.

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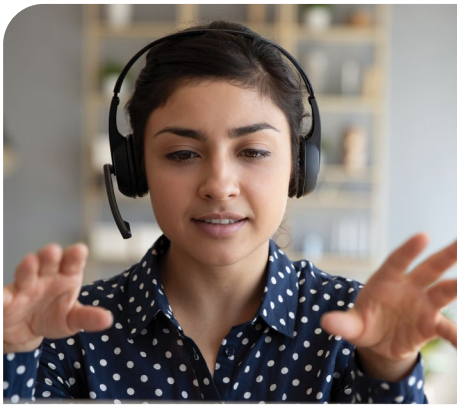

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