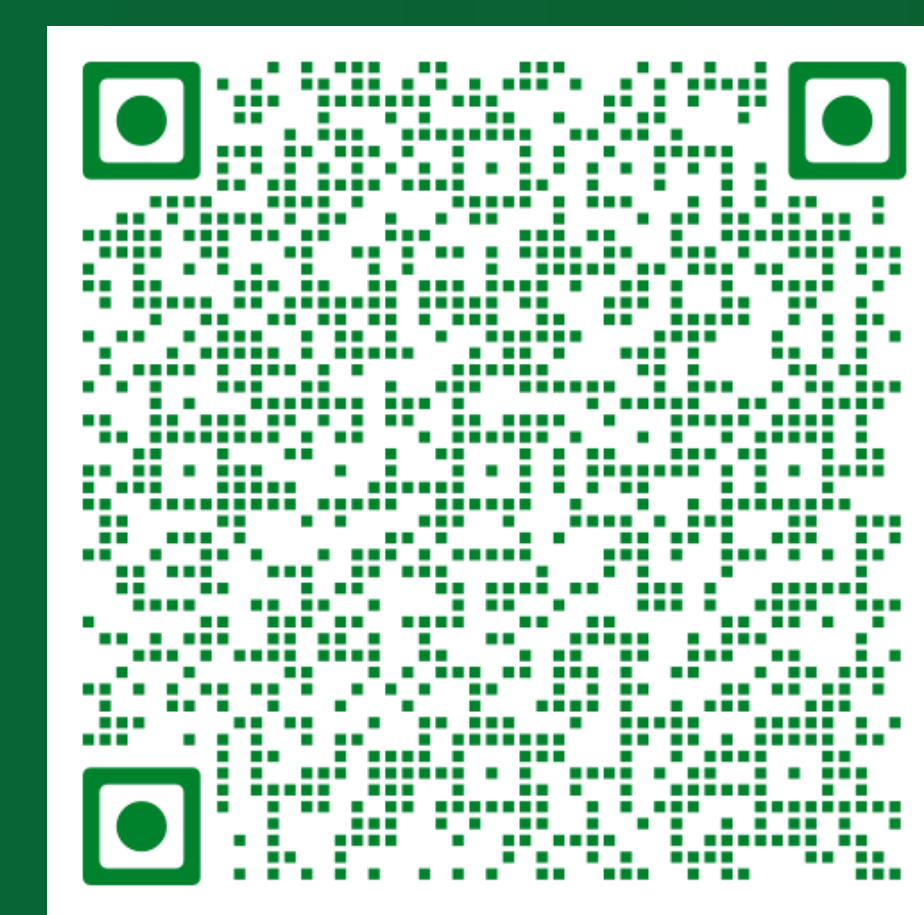




An Optimized Solid Phase Extraction Procedure for EPA Method 8081 and 8082 Analytes in Water

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INTRODUCTION

EPA methods 8081, organochlorine pesticides (OCPs) by GC, and 8082, polychlorinated biphenyls by GC (PCBs), are hazardous waste test methods (SW-846) regulated under the Resource Conservation and Recovery Act (RCRA). These methods are performance based which allow analysts to modify the sampling and analytical approaches to meet the measurement requirements. In other words, these methods convey “what” needs to be accomplished but not prescriptively “how”. For water samples in methods 8081 and 8082, liquid-liquid extraction and solid phase extraction (SPE) are allowed to extract the target analytes from various aqueous samples. EPA method 3535A outlines several solid phase extraction methods for different EPA methods including 8081 and 8082. Use of C18 SPE disk for sample extraction and elution with methylene chloride (DCM), a toxic chlorinated solvent which needs to be solvent exchanged to n-hexane prior to GC-ECD analysis. Method 3535A is also a performance-based SW-846 method that allows for method modifications. In this poster, we have explored a new elution solvent approach in order to eliminate DCM from the extraction protocol.

SPE PROCEDURE

STEP 1: Sample Prep

- Fill sample bottles with 1 liter of water and spike with 5 mL of concentrated sulfuric acid to adjust the pH to less than 2
- Add 100 µl of standard to the samples

STEP 2: Condition

- Setup the HydraFlow® with UCT ECUNIC18 cartridges
- Add 10 mL of acetone to the cartridges, allow them to soak for 2 minutes, then draw to organic waste
- Repeat (b) with 10 mL of hexane and allow the hexane to completely dry out
- Repeat (b) with 10 mL of methanol
- Before all the methanol is pulled through the cartridges, close the valves, add 30 mL of DI water, soak for 2 minutes, then pull to aqueous waste down to 20 mL

STEP 3: Sample Loading

- Close all valves and add samples bottles to the bottle holders
- Slowly run the samples through the cartridges at a rate no faster than 30 mL/minute
- Once the entire sample is run through, allow the cartridges to dry under full vacuum for 15 minutes
- While drying, shake/tap the cartridges to remove excess water
- Once fully dry, analyte elution can begin

STEP 5: Evaporate

- Insert collection vials into the UCT SpEVP
- Dry samples down to 1 mL at 40°C with a gentle nitrogen stream
Note: Do not let the samples evaporate to dryness. This will result in analyte recovery loss.
- Transfer the sample to an autosampler vial to analyze on GC-ECD or GC-MS

STEP 4: Elute

- Rinse the sample bottles with 5 mL of acetone and elute
- Eluate should be collected slowly at a drop-wise rate
- Repeat (a and b) 3 more times with 10 mL of hexane
- The final elution volume should be 5 mL of acetone and 30 mL of hexane, 35 mL total
- Pack Pyrex funnels with glass wool and add 15 grams of sodium sulfate
- Rinse the sodium sulfate with 10 mL of hexane and collect as waste
- Insert the funnels into new 70 mL collection vials
- Pour the sample over the sodium sulfate and break up any clumping with a glass stir rod
- Rinse the collection vial with 10 mL of hexane and pour over the sodium sulfate
- Repeat (i) 2 more times, breaking up clumping between each rinse, for a total solvent volume of 65 mL

REFERENCES

- <https://www.epa.gov/sites/production/files/2015-12/documents/8081b.pdf>
- <https://www.epa.gov/sites/production/files/2015-07/documents/8082a.pdf>
- <https://www.epa.gov/sites/default/files/2015-12/documents/3535a.pdf>

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PCBs: GC-ECD INSTRUMENT PARAMETERS

Column	RTX-PCB	
Front Inlet		
Mode	Split	
Initial Temp	250°C	
Pressure	3.54 Psi	
Split Ratio	10:1	
Split Flow	10.7 mL/min	
Gas Type	Hydrogen	
Detector (µECD)		
Temperature	250°C	
Makeup Flow	60.0 mL/min	
Makeup Gas Type	Nitrogen	
Temperature program		
Rate (°C/min)	Final Temperature (°C)	Hold Time (min)
Initial	100	1
10	320	5

OCPs: GC-ECD INSTRUMENT PARAMETERS

Column	RTX-PCB		
Front Inlet			
Mode	Split		
Initial Temp	250°C		
Pressure	4.28 Psi		
Split Ratio	10:1		
Split Flow	10.7 mL/min		
Gas Type	Hydrogen		
Detector (μECD)			
Temperature	250°C		
Makeup Flow	60.0 mL/min		
Makeup Gas Type	Nitrogen		
Temperature program			
Rate (°C/min)	Final Temperature (°C)		Hold Time (min)
Initial	150		1
10	220		6
2	250		1
10	320		5

PCBs CHROMATOGRAMS

Fig 1. PCBs GC-MS Chromatogram – 1 µg/L

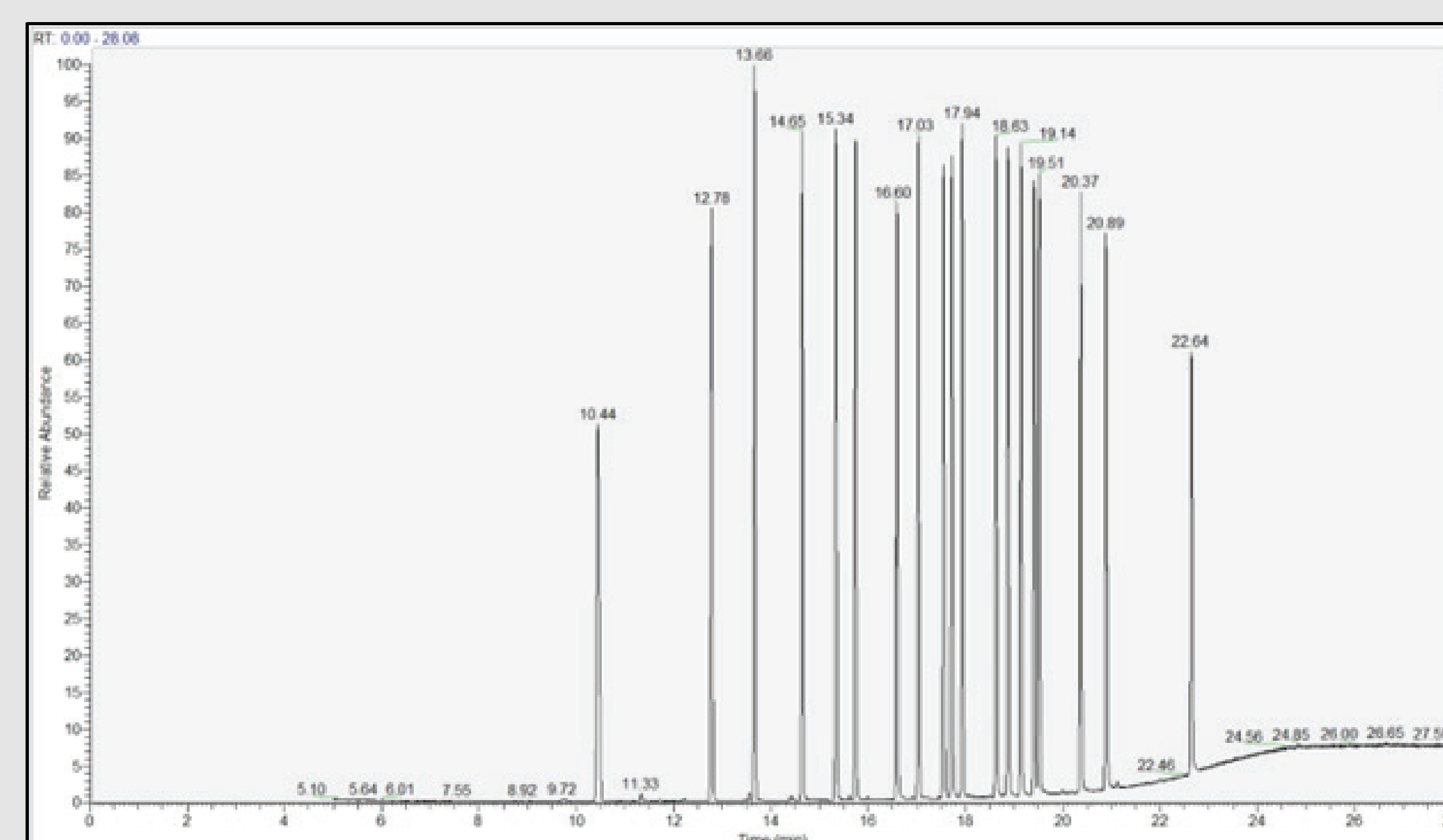


Fig 2. PCBs GC-MS Chromatogram – 1 µg/L (Zoomed in)

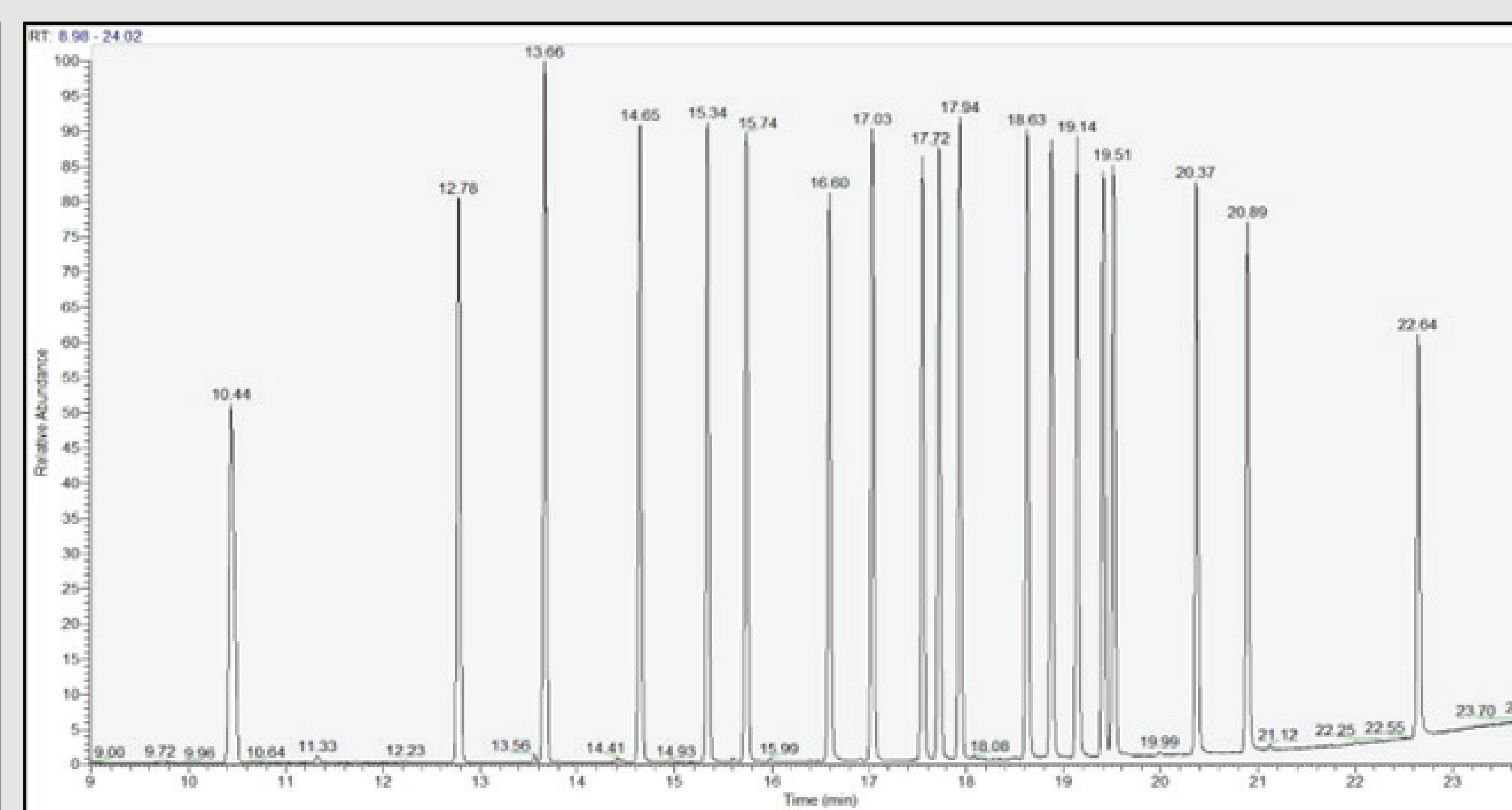


Fig 3. PCBs GC-ECD Chromatogram – 1 µg/L

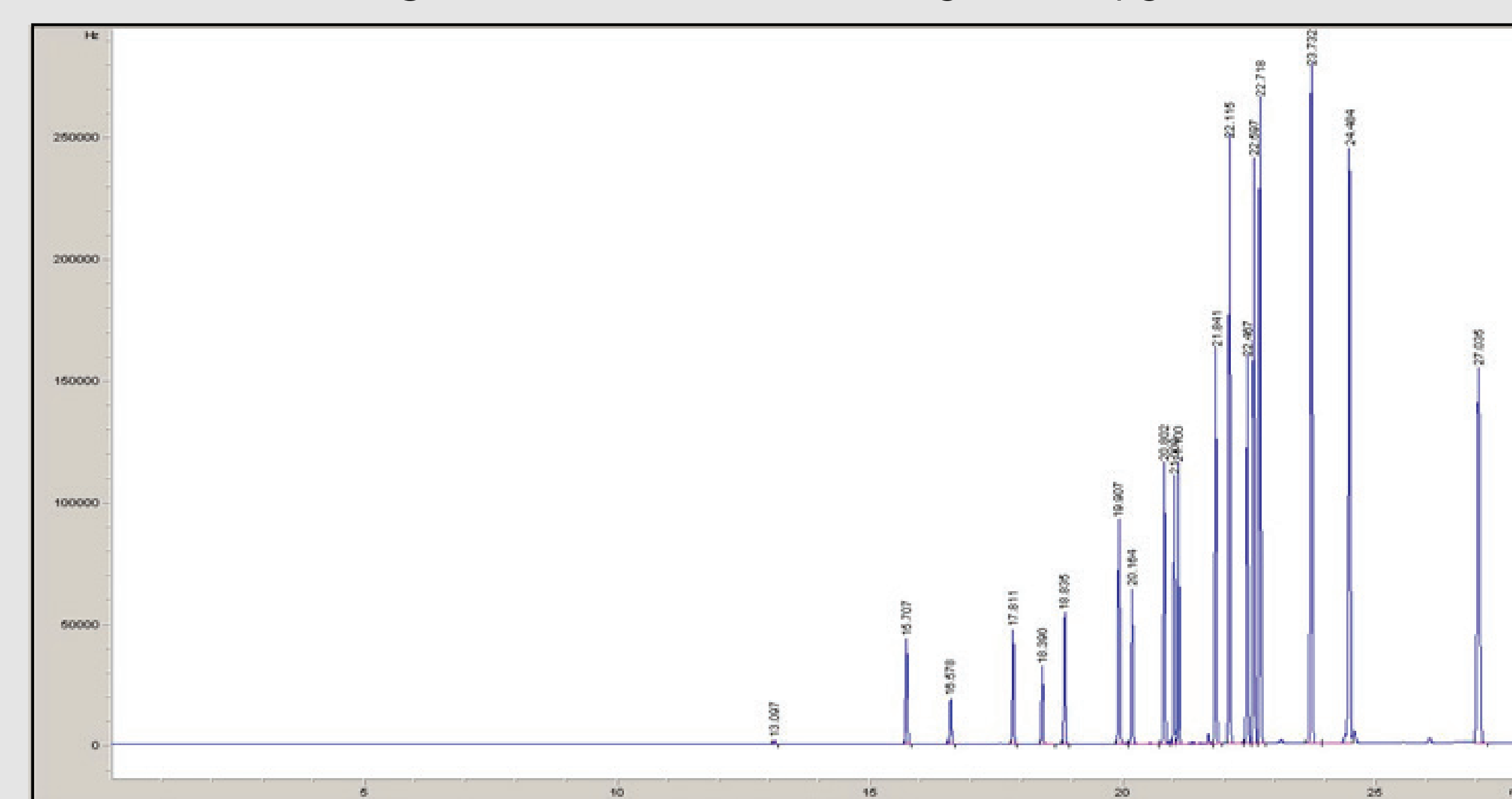
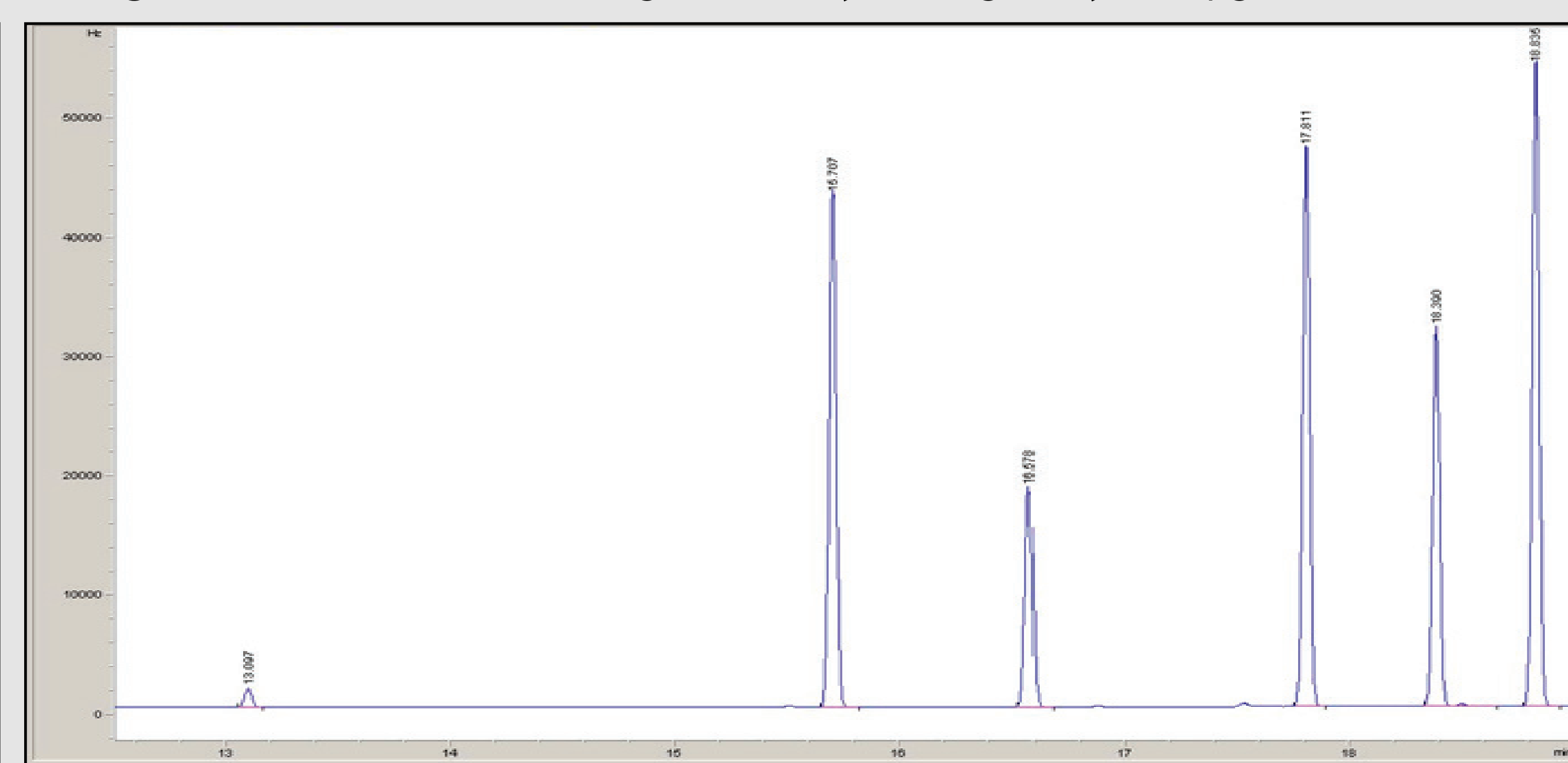


Fig 4. PCBs GC-ECD Chromatogram – Early eluting analytes 1 µg/L (Zoomed in)



OCPs CHROMATOGRAMS

Fig 1. OCPs GC-MS Chromatogram – 1 µg/L

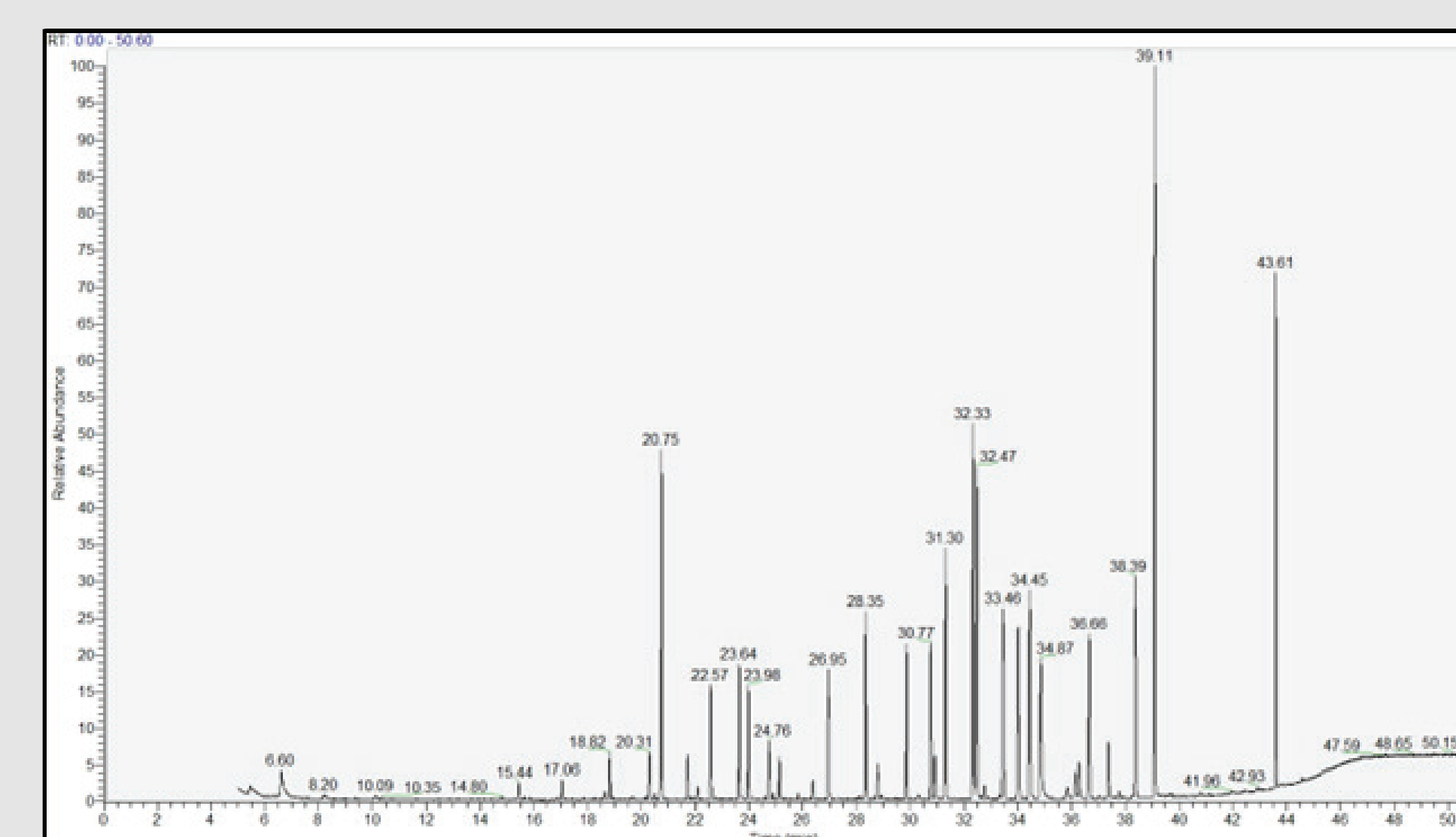


Fig 2. OCPs GC-MS Chromatogram – 1 µg/L (Zoomed in)

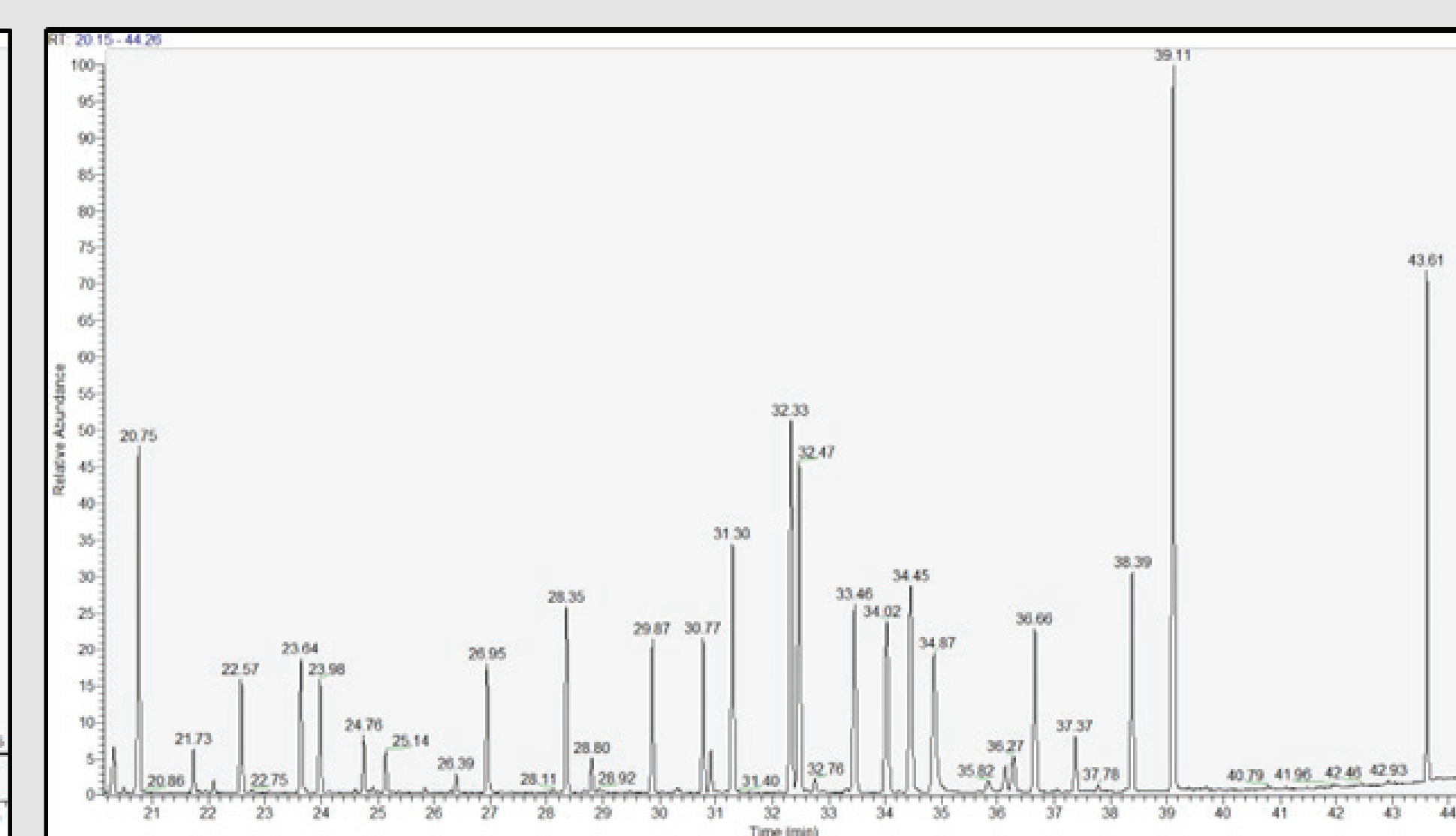
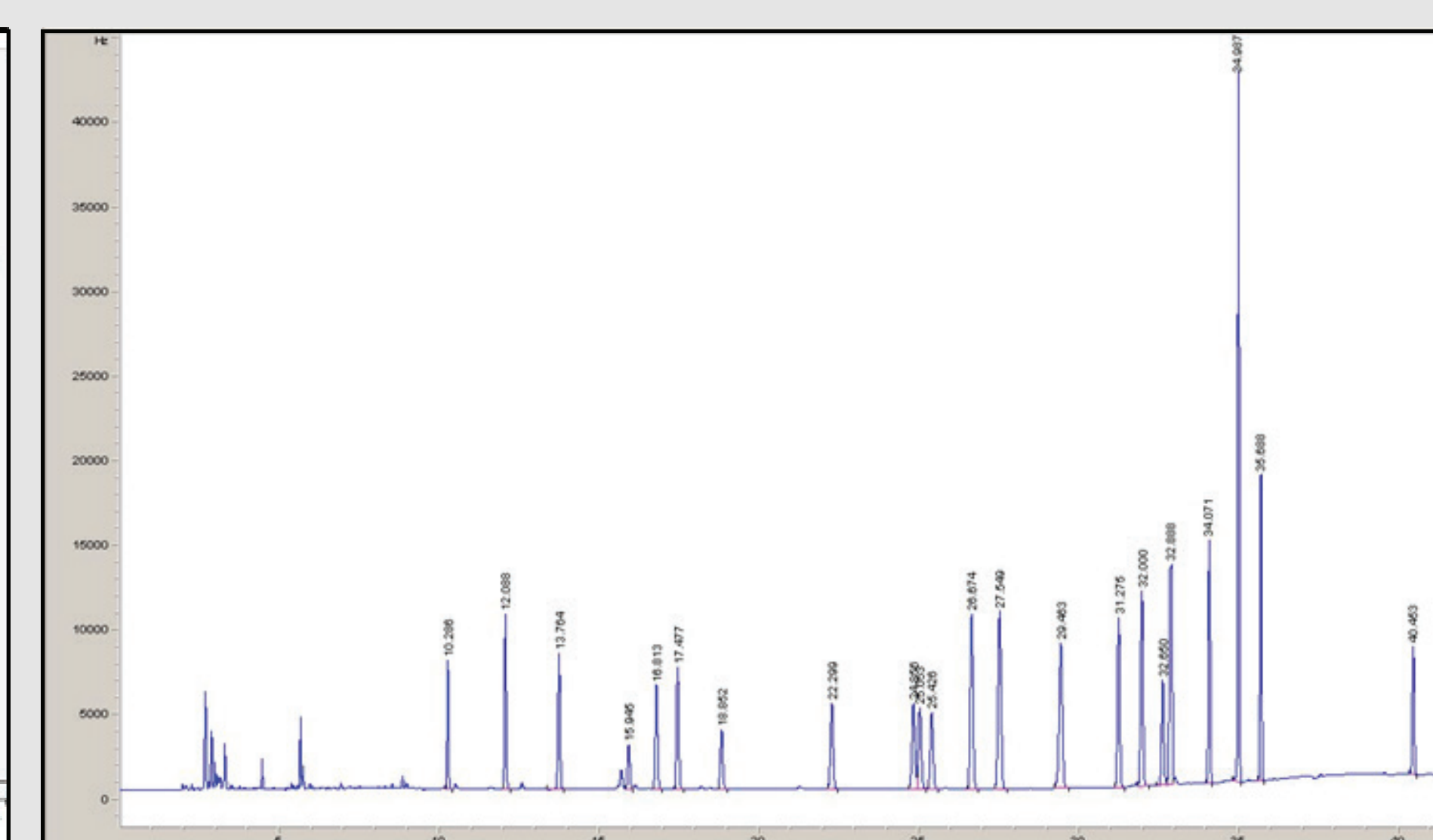


Fig 3. OCPs GC-ECD Chromatogram – 1 µg/L Extracted Standard



RESULTS

PCBs:

Analytes	GC-EDC-RT	GC-MS-RT	Recovery %	RSD %
2-Chlorobiphenyl	13.09	10.44	104.3	6
2,3-Dichlorobiphenyl	15.71	12.78	87.2	10
2,2',5-Trichlorobiphenyl	16.59	13.66	118.2	9
2,4',5-Trichlorobiphenyl	17.82	14.65	126.3	7
2,2',5,5'-Tetrachlorobiphenyl	18.40	15.34	112.1	6
2,2',3,5'-Tetrachlorobiphenyl	18.84	15.74	108.3	6
2,3',4,4'-Tetrachlorobiphenyl	19.92	16.60	94.6	4
2,2',4,5,5'-Pentachlorobiphenyl	20.17	17.03	100.1	6
2,2',3,4,5'-Pentachlorobiphenyl	20.81	17.55	97.6	6
2,3,3',4',6-Pentachlorobiphenyl	21.11	17.72	98.4	6
2,2',3,5,5',6-Hexachlorobiphenyl	21.01	17.94	100.3	6
2,2',4,4',5,5'-Hexachlorobiphenyl	21.85	18.63	90.2	4
2,2',3,4,5,5'-Hexachlorobiphenyl	22.12	18.87	95.5	6
2,2',3,4,4',5'-Hexachlorobiphenyl	22.48	19.14	95.3	5
2,2',3,4',5,5',6-Heptachlorobiphenyl	22.61	19.40	95.1	5
2,2',3,4,4',5'-Heptachlorobiphenyl	22.73	19.51	107.0	6
2,2',3,4,4',5,5'-Heptachlorobiphenyl	23.74	20.37	95.7	6
2,2',3,3',4,4',5-Heptachlorobiphenyl	24.49	20.89	93.7	7
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	27.05	22.64	93.2	5

OCPs:

Analytes	GC-EDC-RT	GC-MS-RT	Recovery %	RSD %
2,4,5,6-tetrachloro-m-xylene	10.28	20.75	83.1	12
α-BHC	12.08	25.10	106.0	10
γ-BHC	13.76	22.58	113.9	10
β-BHC	15.94	23.59	108.7	9
δ-BHC	16.81	23.97	108.4	11
Heptachlor	17.47	26.95	108.5	11
Aldrin	18.85	28.36	123.8	21
Heptachlor epoxide	22.29	29.88	106.7	11
cis-Chlordane	24.85	30.79	107.3	10
trans-Chlordane	25.05	31.31	106.2	10
4,4'-DDE	25.42	32.38	100.9	10
Endosulfan I	26.67	31.42	102.3	11
Dieldrin	27.55	32.48	110.3	11
Endrin	29.46	33.48	97.3	29
4,4'-DDD	31.27	34.44	104.5	12
Endosulfan II	32.00	34.02	109.5	11
4,4'-DDT	32.65	36.66	103.3	10
Endrin aldehyde	32.89	34.86	102.6	12
Methoxychlor	34.07	39.10	99.0	10
Endosulfan sulfate	34.99	36.26	102.2	11
Endrin ketone	35.69	38.38	96.8	3
Decachlorobiphenyl	40.45	43.60	83.6	15

CONCLUSION

This poster describes an optimized SPE procedure using ECUNIC18 SPE cartridges to extract PCBs and OCPs in water samples. This procedure employs acetone and n-hexane mixture as elution solvents instead of methylene-chloride (DCM). After evaporation, the analytes are enriched in n-hexane thus no solvent exchange is needed for GC-ECD detection. The modified method uses non-chlorinated solvents (acetone and n-hexane) to elute the target analytes and surrogates that are retained on the C18 sorbent. Using Sodium sulfate and then rinsing it a few times has substantially improved Aldrin recoveries. Excellent recoveries > 85 % for most of the analytes in the method and RSD% was < 10%. This is a very good method for a high-volume production lab that would like to streamline an SPE extraction. The method was carried out using UCT's new extraction manifold, the HydraFlow®. Many advantages were gained from employing this manifold, one of which is the high vacuum pressure which allows for drying the cartridges. This step is very critical in obtaining acceptable recoveries. Any moisture left in the cartridges can be the root cause behind lower recoveries.