Simultaneous analysis of residual contaminants in drinking water using Programmed Temperature Vaporization (PTV) for Large Volume Injection (LVI) and GC-MS/MS

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1. Overview

Control and prevention of environmental pollution have emerged as paramount global concerns. Activities like industrial discharge, agricultural run-off, and improper waste disposal introduce a wide range of contaminants into various water bodies including drinking water.
Despite the multiple treatments and filtration processes that drinking water (Figure 1) undergoes before reaching consumers, the accurate quantitation of the target contaminants is of great importance. This involves tedious extraction and concentration processes followed by instrumental analysis.

Figure 1 Drinking Water

2. Introduction

This study aimed to develop a single analytical method for the simultaneous analysis of over 60 residual contaminants, including Poly-Aromatic Hydrocarbons (PAH), Poly-Chlorinated Biphenyls (PCB), and pesticides, in drinking water. Traditionally, multiple methods are being employed for analyzing these contaminants. Most common ones include, extraction using solvents in large separating funnel or SPE cartridge followed by volume concentration by evaporation. These methods require huge sample and solvent quantities. Due to these factors like large sample size handling, concentration steps etc., method may show poor reproducibility.

By utilizing Programmed Temperature Vaporization (PTV) for Large Volume Injection (LVI), the method significantly reduces the initial sample amount required for preparation, pre-treatment steps, and solvent consumption compared to conventional approaches, while eliminating the need for final sample concentration. The optimized procedure achieved limits of quantification (LOQs) as low as 0.005 ppb and 0.05 ppb, demonstrating high sensitivity without compromising efficiency.

Validation parameters like specificity, linearity, recovery and precision were studied as per SANTE guidelines[1]. For linearity and recovery study, matrix match calibration was used.

3. Materials and methods

For this study, reference standard mixtures of over 60 contaminants regulated in drinking water were procured from Restek® Corporation. It included PAH, PCB and GC amenable pesticides.
Drinking water sample was extracted and used to prepare matrix-matched calibration standards and spiked samples. This method was validated for criteria mentioned in SANTE Guidelines.
GCMS-TQ8040 NX (Figure 2), manufactured by Shimadzu Corporation Japan, was used to quantify residual contaminants in drinking water sample.

3-1. Method development

Instrumental method was developed based on chromatographic and mass spectrometric parameters. Use of Smart Environmental Database (for PAH, PCB) and Smart Pesticides Database Ver.2 (for Pesticides) enabled quick instrumental method optimization for higher throughput. For all the contaminants, 1 target and 2 reference MRM transitions were included in the method. Shimadzu's 'LabSolutions Insight' software was used for data processing, which helped in evaluating validation parameters with ease. This greatly reduced the method development and optimization time. Pretreatment method involved use of small sample quantity and simple extraction process for better and consistent recoveries.

3-2. Sample and standard preparation

Locally purchased drinking water sample was used for this study. 30 mL of sample was extracted using 3 mL of dichloromethane (DCM) solvent along with pre-heated sodium chloride (AR grade) in optimized proportion to maximize recoveries of contaminants at trace level. The mixture was vortexed for 2 minutes. The mixture was allowed to settle. Following this, 2 mL of lower DCM layer was collected with gas tight syringe and transferred into glass vial. To this, 50 mg anhydrous sodium sulphate was added and mixed well. Then the supernatant layer of DCM was removed, filled in GC vial and injected. During extraction itself, the sample was concentrated 10 times avoiding additional evaporation & reconstitution steps. All samples were analyzed as per conditions shown in table 1.

Preparation of solvent standard concentration levels

The PAH, PCB, and multi-residue pesticides mixtures were mixed and diluted using ethyl acetate to prepare 'Standard Mixture Stock Solution' of about 1000 ppb. From this, seven concentration levels of 0.25 ppb to 100 ppb were prepared using DCM.

• Preparation of matrix matched standard linearity levels

The blank sample extract (matrix blank) prepared as per section 3-2 was used as a diluent. It was spiked with above solvent standard levels to prepare matrix match linearity of 0.025 to 10 ppb. It was ensured that the v/v proportion of matrix blank and solvent standard is kept same to keep the matrix effect constant throughout the linearity levels.

• Preparation of spike samples (Recovery samples)

To determine the extraction efficiency of the method, recovery study was conducted. For this, 30 mL sample was spiked with 'Standard Mixture Stock Solution' to prepare recovery samples of 0.005 and 0.05 ppb. The spiked analytes were then extracted, analyzed and quantified against matrix matched linearity to study their recoveries. As the sample is 10 times concentrated during extraction, the actual concentration injected on instrument will be 10-fold.

3-3. Analytical Conditions

Table 1 Instrument configuration and Analytical Conditions: GC-MS/MS

System Configuration	
Instrument	: GCMS-TQ8040 NX
Auto-injector	: AOC™-20i + s
Column	: SH-I-5Sil MS (30 m × 0.25 mm I.D., df = 0.25 µm) (P/N:221-75954-30)
Liner	: Restek® Topaz PTV Liner, with wool
GC	
Injection Type	: PTV
Injector temp. program	: 45 °C (0.50 min), 400 °C/min to 330 °C (63 min), -400 °C/min to 45°C (0.28 min)
Column oven temp	: 35 °C (5 min), 30 °C/min to 120 °C (0 min), 4 °C/min to 330 °C (3.67 min)
Run time	: 55 min
Injection mode	: Split (Split Ratio: 5)
Injection volume	: 50 µL (5 µL x 10 Multi-Injection Counts)
Carrier gas	: He
Column Flow	: 2.00 mL/min (Constant mode)
MS	
Interface temp.	: 330 °C
Ion source temp.	: 250 °C
Ionization mode	: EI
Solvent cut time	: 7.5 min
Loop Time	: 0.3 sec

Table 2 Summary results

ID	Compound Name	Ret. Time (min)	Target MRM (m/z)	CE	(r^2)	LOQ (ppb)	% Mean Rec @ LOQ (n=6)	% RSD_R @ LOQ (n=6)
1	Napthalene	9.677	128.10>102.10	20	0.4136	NA*	-	-
2	Acenaphthylene	13.766	152.10>126.10	28	0.9770	0.05	119.00	4.65
3	Acenaphthene	14.464	153.10>151.10	28	0.9982	0.05	118.92	4.27
5	Fluorene	16.538	165.10>163.10	28	0.9392	NA*	-	-
12	Anthracene	20.997	178.10>152.10	20	0.9960	NA*	-	-
14	Phenanthrene	21.230	258.00>186.00	25	0.9761	0.005	87.08	18.26
26	Fluoranthene	27.372	202.10>152.10	28	0.9946	0.05	116.61	7.22
30	Pyrene	28.486	200.10>198.10	30	0.9832	0.05	120.02	3.62
52	Benz(a)anthracene	35.421	228.10>226.10	28	0.9804	0.005	119.52	5.29
53	Chrysene	35.622	228.10>226.10	28	0.9899	0.05	118.42	3.49
55	Benzo(b)fluoranthene	41.186	252.10>250.10	28	0.9692	0.005	113.59	9.10
56	Benzo(k)fluoranthene	41.315	252.10>250.10	28	0.9715	0.005	113.43	11.68
58	Benzo(a)pyrene	42.675	252.10>250.10	28	0.9815	0.005	115.34	6.79
59	Indeno[1,2,3-cd]pyrene	47.738	276.10>275.10	28	0.9910	0.05	118.69	3.72
60	Dibenz(a,h)anthracene	47.979	278.10>276.10	30	0.9742	0.05	119.37	3.73
61	Benzo(ghi)perylene	48.696	276.10>274.10	34	0.9899	0.05	118.61	2.28
6	Phorate	19.095	260.00>75.00	8	0.9086	0.05	116.55	17.47
7	BHC-alpha (benzene hexachloride)	19.158	180.90>144.90	16	0.9919	0.005	115.65	2.77
9	Hexachlorobenzene	19.474	283.80>213.80	28	0.9798	0.005	111.81	3.17
10	BHC-beta	20.414	180.90>144.90	16	0.9859	0.005	116.67	4.68
11	BHC-gamma (Lindane, gamma HCH)	20.642	180.90>144.90	16	0.9759	0.005	111.02	6.02
15	BHC-Delta	21.781	180.90>144.90	16	0.9848	0.005	119.42	2.67
17	Parathion-methyl	23.727	125.00>47.00	12	0.9843	0.005	118.06	4.14
18	Heptachlor	23.872	271.80>236.90	20	0.9768	0.005	111.79	4.07
19	Alachlor	24.143	188.10>160.10	10	0.9830	0.05	117.94	6.45
22	Chlorpyrifos	26.051	313.90>257.90	14	0.9964	0.05	119.01	3.87
23	Parathion	26.072	291.10>109.00	14	0.9806	0.05	119.34	2.90
24	Aldrin	26.685	262.90>193.00	28	0.9860	0.05	118.07	7.53
25	Heptachlor exo-epoxide (isomer B)	27.265	352.80>262.90	14	0.9831	0.005	104.84	16.09
27	Heptachlor endo-epoxide (isomer A)	27.457	354.80>253.00	18	0.9908	0.05	115.89	6.31
29	Chlordane-trans (gamma)	28.334	372.80>263.90	28	0.9863	0.005	112.00	6.99
31	DDE-o,p'	28.735	246.00>176.00	30	0.9917	0.005	118.10	3.67
32	Endosulfan I (alpha isomer)	28.843	194.90>160.00	8	0.9901	0.05	119.77	5.47
34	Chlordane-cis (alpha)	29.031	374.80>265.90	26	0.9728	0.005	95.17	8.24
35	Butachlor	29.385	262.90>193.00	34	0.9984	0.05	85.82	8.85
36	Dieldrin	30.004	188.10>132.10	18	0.9827	0.05	115.55	7.36
38	DDE-p,p'	30.194	246.00>176.00	30	0.9732	0.005	116.93	4.66
40	DDT-o,p'	30.525	235.00>165.00	24	0.9939	0.005	118.30	4.86
42	Endosulfan II (beta isomer)	31.378	194.90>160.00	8	0.9947	0.05	117.46	6.58
43	DDD-o,p'	32.026	235.00>165.00	24	0.9896	0.005	118.73	3.51
44	DDD-p,p'	32.128	235.00>165.00	24	0.9908	0.005	118.32	5.11
47	Endosulfan sulfate	33.294	271.80>236.90	18	0.9900	0.005	106.75	8.74
48	DDT-p,p'	33.655	235.00>165.00	24	0.9830	0.005	113.49	5.26
4	2-Chlorobiphenyl (BZ #1)	14.756	188.00>153.10	10	0.9883	0.05	116.54	3.72
8	2,3-Dichlorobiphenyl (BZ #5)	19.233	222.00>152.10	25	0.9814	0.05	119.93	3.88
13	2,2',5-Trichlorobiphenyl (BZ #18)	21.158	178.10>152.10	20	0.9649	0.005	106.63	2.57
16	2,4',5-Trichlorobiphenyl (BZ #31)	23.242	258.00>151.00	50	0.9878	0.005	119.09	10.83
20	2,2',5,5'-Tetrachlorobiphenyl (BZ #52)	24.907	289.90>219.90	25	0.9871	0.05	119.87	1.10
21	2,2',3,5'-Tetrachlorobiphenyl (BZ #44)	25.820	289.90>219.90	30	0.9778	0.005	117.11	5.22
28	2,3,4,4'-Tetrachlorobiphenyl (BZ #60)	27.762	289.90>219.90	25	0.9845	0.005	119.39	4.30
33	2,2',3',4,5-Pentachlorobiphenyl (BZ #97)	28.858	327.90>255.90	25	0.9965	0.05	119.15	2.98
37	2,2',4,5,5'-Pentachlorobiphenyl (BZ #101)	30.018	327.90>292.90	15	0.9929	0.005	103.97	17.04
39	2,3,3',4,6-Pentachlorobiphenyl (BZ #109)	30.459	325.90>255.90	30	0.9892	0.005	116.81	2.96
41	2,2',3,5,5',6-Hexachlorobiphenyl (BZ #151)	31.018	361.90>289.90	30	0.9918	0.005	118.74	5.87
45	2,2',4,4',5,5'-Hexachlorobiphenyl (BZ #153)	32.645	361.90>289.90	25	0.9648	0.005	118.79	2.55
46	2,2',3,4',5,5'-Hexachlorobiphenyl (BZ #146)	33.178	359.90>289.90	30	0.9896	0.005	119.53	0.81
49	2,2',3,4,4',5-Hexachlorobiphenyl (BZ #137)	33.821	361.90>289.90	25	0.9853	0.005	118.04	4.21
50	2,2',3,4,4',5',6-Heptachlorobiphenyl (BZ #183)	34.569	395.80>323.80	30	0.9953	0.005	116.71	4.78
51	2,2',3,4',5,5',6-Heptachlorobiphenyl (BZ #187)	34.787	395.80>323.80	30	0.9902	0.005	118.22	2.89
54	2,2',3,3',4,4',5-Heptachlorobiphenyl (BZ #170)	36.750	358.80>323.80	0	0.9810	0.005	115.42	5.44
57	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (BZ #206)	42.190	463.80>393.70	30	0.9891	0.005	116.37	2.38

* Analytes incurred in large amounts in blanks sample, hence LOQ could not be determined

PAH Pesticides PCB

Figure 2. Shimadzu GCMS-TQ8040 NX

4. Results

Validation parameters like linearity, recovery and precision were studied to establish LOQs. The summary results are shown in Table 2.

4-1. Linearity

For linearity study and quantifying spiked samples, matrix matched calibration standards were used. Multilevel calibration curve included 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5 and 5 ppb concentration levels. All calibration standards were found within 80 to 120% accuracy range which is well within the criteria mentioned in SANTE guidelines.

4-2. Recovery

Recovery was evaluated by quantifying spiked samples at 0.005 and 0.05 ppb (six spiked samples at each level) against matrix matched linearity. Mean recoveries were found to be within 80-120% at LOQ level (Refer Table 2). As mentioned previously, spiked samples were concentrated 10 times, so that final concentrations were comparable to 0.05 and 0.5 ppb of linearity runs.

4-3. Reproducibility (% RSD_R)

Reproducibility experiment for recoveries was performed on 6 different spiked samples at 0.005, and 0.05 ppb concentration levels. The % RSD of 6 spiked samples at their respective LOQ level was found to be less than 20 % (Refer Table 2).

4-4. LOQ

Out of 61 contaminants analyzed, this method successfully achieved LOQs of 0.005 and 0.05 for 36 and 22 contaminants, respectively. Remaining three contaminants all from PAH category were incurred in high amounts in blanks, hence their validation parameters could not be studied. List of LOQs of individual contaminants is shown in Table 2.

5. Conclusion

- This study shows that the extraction of reduced sample quantity combined with LVI of 50 µL on GC-MS/MS system is a reliable and efficient tool to simultaneously quantify residual contaminants like PAH, PCB and pesticides in drinking water sample.
- Also, highly sensitive Shimadzu GC-MS/MS allows trace level detection even without the need of evaporating & concentrating the sample. This helps in ruggedness resulting in reproducible detection of analytes.
- The combination of sensitive instrument and reproducible extraction method enables its use in testing laboratories for residual contaminants analysis in drinking water.

6. References

1. Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed. SANTE/11312/2021