

1. Introduction

The present problem of pesticide in aquatic environment are receiving worldwide concern as pesticide tends to accumulate in the body of the aquatic organism and sediment soil, posing health risks to the human. The occurrence of pesticides in the water body is derived by the runoff from the agricultural field and industrial wastewater. Soluble pesticides were carried away by water molecules especially during the precipitation event by percolating downward into the soil layers and eventually reach surface waters and groundwater. Consequently, it degrades water quality and reduces the supply of clean water for potable water. Long-time exposure to the low concentration of pesticides had resulted in non-carcinogenic health risks. The conventional method of pesticide treatment processes encompasses coagulation-flocculation, adsorption, filtration and sedimentation, which rely on the phase transfer of pollutants. Those methods are having high operational cost and may cause secondary pollution such as sludge formation.

ASTM D-7645 is performance-based method. The samples are spiked with the surrogate standard and filtered using syringe filter and analyzed directly on LC-MS/MS. This procedure covers the determination of Aldicarb, Aldicarb sulfone, Aldicarb sulfoxide, carbofuran, methomyl, oxamyl and thiofanox (referred to collectively as carbamates in this test method) [1].

This highly sensitive method was developed to cover carbamates in water by direct injection using Shimadzu LCMS-8045, a liquid chromatography mass spectrometry detector as per the ASTM D-7645. These analytes are qualitatively and quantitatively determined by this test method. The structures of carbamates are shown in Figure 1. Carbofuran-D3 (Surrogate standard) was used for the analysis to monitor recovery for all the samples tested. All the glassware were washed properly with hot water and solvents to reduce the interference.

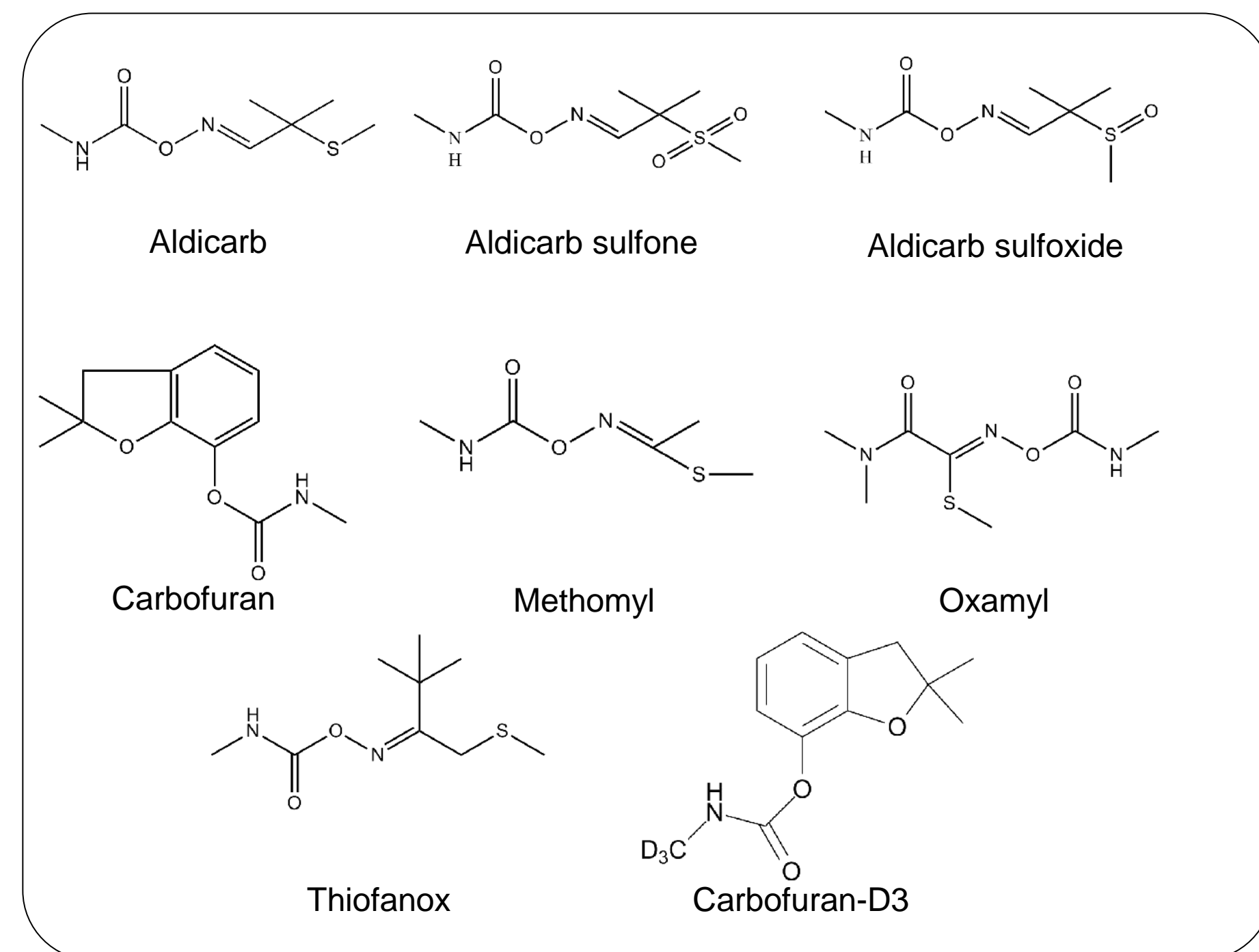


Figure 1. Structure of carbamates and surrogate standard.

2. Materials and methods

2-1. Sample preparation

Calibration standard solutions were prepared containing 9 concentration levels of carbamates and carbofuran-D3 surrogate prior to the analysis. The certified mix calibration standard stock in methanol was purchased and from that the intermediate stock of 1 ppm was prepared in water. From this standard stock solution, the nine level of calibration standard solutions were prepared in water. The concentrations of the calibration solutions of 0.5 ppb, 1 ppb, 5 ppb, 10 ppb, 25 ppb, 50 ppb, 75 ppb, 100 ppb, and 250 ppb were prepared. The calibration curve was plotted with external standard method.

Three different types of water samples of 25 mL (Tap water, RO water and bottled water) were spiked by adding 25 µL of stock solution of 50 ppm, which results into the 50 ppb recovery solutions.

A surrogate standard stock solution containing carbofuran-D3 is added to all samples. A stock surrogate spiking solution of 50 ppm was prepared in water from the 100 ppm certified standard in methanol. To 25 mL of each sample, added 25 µL of 50 ppm stock solution. Samples were filtered through 0.45 µm syringe filter. Transferred the filtrate in to the HPLC vial for the analysis.

MRM was optimised for all the ions to ensure the best response of the LC-MS/MS system using LabSolutions software. C18 mode of separation was used for the analysis. The detailed LC and MS parameters are shown in Table 1.

2-2. LC-MS/MS analysis



Figure 2. Nexera with LCMS-8045

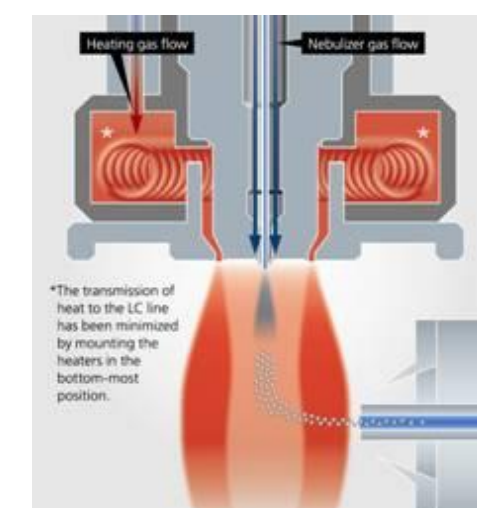


Figure 3. Heated ESI probe

LCMS-8045 triple quadrupole mass spectrometer by Shimadzu (shown in Figure 2), sets a new benchmark in triple quadrupole technology with an unsurpassed sensitivity (UF sensitivity), ultra fast scanning speed of 30,000 u/sec (UF scanning) and polarity switching speed of 5 msec (UF switching). This system ensures highest quality of data, with very high degree of reliability.

In order to improve ionization efficiency, the newly developed heated ESI probe (shown in Figure 3) combines high-temperature gas with the nebulizer spray, assisting in the desolvation of large droplets and enhancing ionization. This development allows high-sensitivity analysis of a wide range of target compounds with considerable reduction in background.

Table 1. Instrument parameters

MS Parameters (LCMS-8045)	
MS interface	Electro Spray Ionization (ESI)
Gas flow	Nebulizing gas:- 3 L/min; Drying gas:- 10 L/min; Heating gas:-10 L/min
MS temperatures	Desolvation line:- 150 °C; Heating block:- 200 °C

MS Parameters (LCMS-8045)

MRM transition (positive)

Aldicarb	208.10>116.00	Methomyl	163.10>88.10
Aldicarb Sulfone	240.20>148.10	Oxamyl	237.30>72.10
Aldicarb Sulfoxide	207.10>89.10	Thiofanox	241.10>184.00
Carbofuran	222.30>165.10	Carbofuran D-3	225.20>165.10

UHPLC condition

Column	Shim-Pack Velox SP-C18 2.7 µm (P/N 227-32003-03)
Mobile phase	A: 95% water/ 5% methanol, 5mM ammonium formate B: 95% methanol/ 5% water, 5mM ammonium formate
Flow rate	0.4 mL/min
Elution mode	Gradient as per ASTM D-7645
Injection vol.	5 µL
Column temperature	40 °C

3. Results

The prepared calibration standards were injected on LCMS and plotted the calibration curve for a 6 carbamates and surrogate standard. The linear calibration curve were used for all the analytes from 0.5 ppb to 100 ppb, and the calibration coefficient (r^2) was found to be more than 0.99. The 1/C weighing method was used to give more emphasis to lower concentrations. Detection Verification Level (DVL) of 0.250 ppb solution was prepared as per the guidelines of reference method to check the lower detection limit. Prepared and injected 50 ppb of recovery solutions and surrogate spiked samples in duplicates. The 0.250 ppb DVL solution chromatograms are shown in Figure 4. The calibration curves from 0.5-100 ppb are shown in Figure 5. The recovery sample passes the criteria set by ASTM method. The surrogate standard spike in each sample solution produced acceptable results. The results of recovery and sample spiked with surrogate are given in Table 2 and 3, respectively.

The method established here is capable of giving much lower detection limits than the reference method with the injection volume is 10 times lower than the ASTM method with much higher sensitivity at DVL.

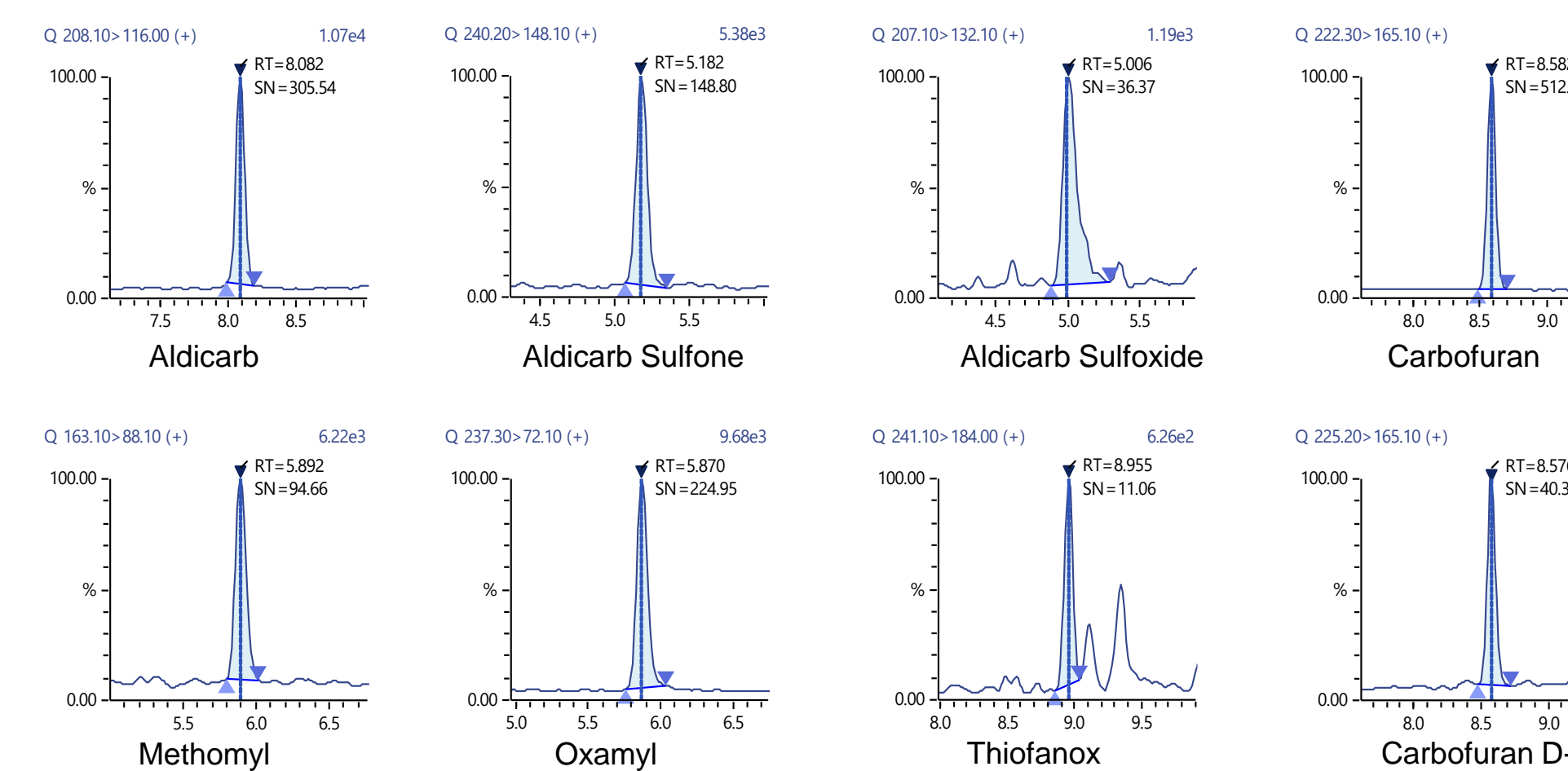


Figure 4. MRM chromatograms of 0.250 ppb standard

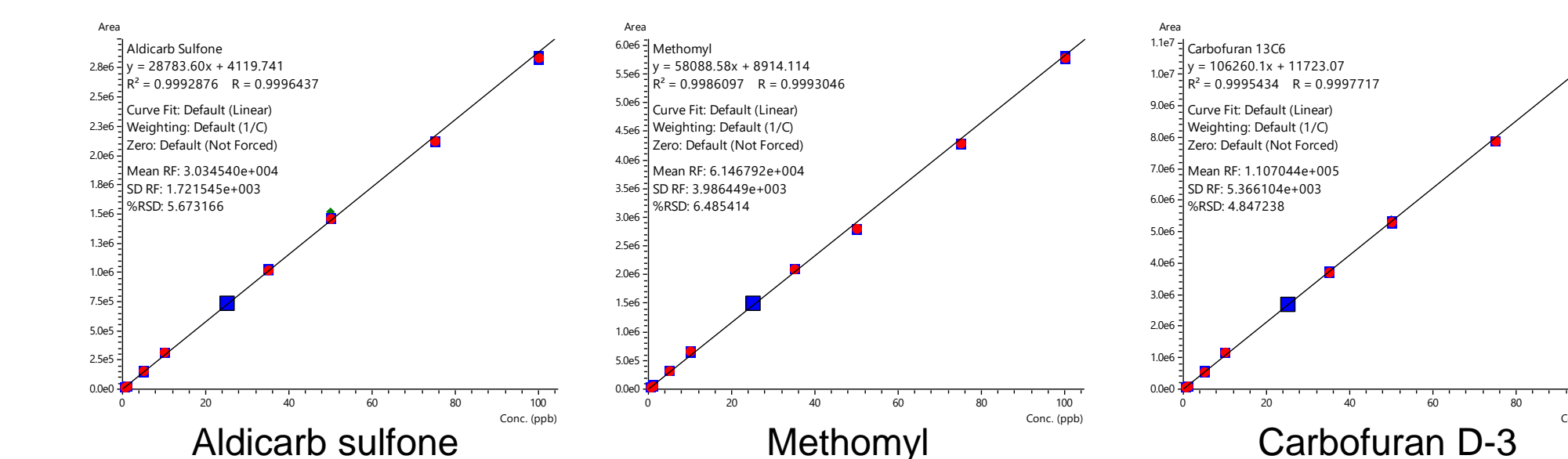


Figure 5. Linearity curve plots of carbamates and surrogate standard

Table 2. Results of accuracy, regression and detection level

Analyte	% Accuracy at 0.5 ppb	r^2	S/N at 0.5 ppb
Aldicarb	96.64	0.9954	800.4
Aldicarb sulfone	90.98	0.9993	274.7
Aldicarb sulfoxide	101.0	0.9995	91.90
Carbofuran	92.54	0.9995	1046
Methomyl	83.55	0.9986	272.2
Oxamyl	91.96	0.9995	348.5
Thiofanox	88.74	0.9968	50.30
Carbofuran D-3	89.18	0.9995	137.9

Table 3. Results of recovery and surrogate sample analysis

Analyte	Tap Water	RO water	Bottled water	Matrix spike at 50 ppb
Aldicarb	X	X	X	42.95
Aldicarb sulfone	X	X	X	52.64
Aldicarb sulfoxide	X	X	X	49.61
Carbofuran	X	X	X	49.61
Methomyl	X	X	X	47.64
Oxamyl	X	X	X	50.24
Thiofanox	X	X	X	41.40
Carbofuran D-3	45.92	48.99	55.12	50.73

4. Conclusion

- Highly sensitive LC-MS/MS method is developed for carbamates in water by LCMS-8045 with surrogate spiked samples. LCMS-8045 is capable of detecting carbamates as per the ASTM D-7645.
- This method is almost 20 times more sensitive than the requirements as per the ASTM D-7645.

5. References

- [1] ASTM D-7645:- Determination of Aldicarb, Aldicarb Sulfone, Aldicarb Sulfoxide, Carbofuran, Methomyl, Oxamyl and Thiofanox in Water by Liquid Chromatography/ Tandem Mass Spectrometry (LC/MS/MS)

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