Small scale collaborative trial on the method for the determination of Metolachlor in TC, EC and EW

5318/R

Report to CIPAC
By
Chinese Pesticide Analytical Committee（CHIPAC）

Method Developed by Shandong Binnong Technology Co., Ltd

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Table of Content

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1. Metolachlor method description

1.1 Outline of method

Metolachlor is dissolved in methanol and determined by gas chromatography with flame ionization detection, using dipentyl phthalate as internal standard.

1.2 Apparatus and reagents

GC system with FID

Column, HP-5, capillary, 30 m x 0.32 mm×0.25µm, or equivalent.

Electronic integrator or data system

ultrasonic bath

Nylon syringe filters, 0.22 µm

Metolachlor standard of known purity

Dipentyl phthalate pure, internal standard. Should not contain any impurities that elute at the metolachlor retention time.

Methanol, HPLC grade

Internal standard solution. Weigh into a volumetric flask (250 ml) dipentyl phthalate (2.5 g). Add methanol (200 ml) into the flask, place the flask in an ultrasonic bath for 2-3 min. Allow to cool to ambient temperature. Dilute to volume with methanol. Mix thoroughly.

Calibration solutions. Weigh in duplicate (to the nearest 0.1 mg) into a volumetric flask (10 ml) about 50 mg of metolachlor standard (s mg). Add internal standard solution (5 ml) into the flask, place the flask in an ultrasonic bath for 2-3 min. Allow to cool to ambient temperature. Dilute to volume with methanol. Mix thoroughly. Filter a portion of each sample solution with a 0.22µm filter prior to analysis (Solutions CA and CB).

1.3 GC condition

Column temperature 182°C

Injection port temperature	250°C
Detector temperature	250°C
Injection volume	1.0 µl
Flow rate	
nitrogen (carrier)	2.0 ml/min
hydrogen	30 ml/min
air	300 ml/min
make up	25 ml/min
Injection type	Split
Split ratio	20:1
Retention time	Metolachlor: about 8.6 min
	internal standard: about 15.2 min

1.4 Procedure

(i) Preparation of Metolachlor sample. Weigh in duplicate (to the nearest 0.1 mg) into a volumetric flask (10 ml) sufficient sample to contain about 50 mg of metolachlor (w mg). Add internal standard solution (5 ml) into the flask, place the flask in an ultrasonic bath for 2-3 min. Allow to cool to ambient temperature. Dilute to volume with methanol. Mix thoroughly. Filter a portion of each sample solution with a 0.22µm filter prior to analysis (Solutions S1 and S2).

(ii) Determination of metolachlor

Inject into the gas chromatograph 1µl portions of the calibration solution until the area (or height) ratios (R') of metolachlor to the internal standard varies by less than 1.5% for successive injections, otherwise prepare new calibration solutions. Inject in duplicate 1µl portions of each sample solution bracketing them by injections of the calibration solutions as follows: CA, S1, S1, CB, S2, S2, CA, and so on.

(iii) Calculation

Calculate the mean value of each pair of response factors bracketing the two injections of a sample and use this value for calculating the metolachlor contents of the bracketed

sample injections. The metolachlor content is the mean value of two sample solutions.

$$f_i = \frac{s \times P}{R'}$$

$$\text{Metolachlor content} = \frac{R \times f}{w} \text{ g/kg}$$

where:

R = peak area (or height) ratio of metolachlor to the internal standard for the sample solution

R' = peak area (or height) ratio of metolachlor to the internal standard for the calibration solution

f_i = individual response factor

f = mean response factor

s = mass of metolachlor standard taken (mg)

w = mass of sample taken (mg)

P = purity of the standard metolachlor (g/kg)

2. Participants and sample distribution

Participants

Index	NAME	ORGANIZATION	Address
Lab1	Dong Jie	Shandong Binnong Technology Co., Ltd.	No.518, Yongxin Road, Binbei Town, Binzhou, Shandong, China
Lab2	Shao Xiangdong	BioGuide Technologies Co., Ltd	Building 8, IFST-CAAS, 2 Yuanmingyuan West Road, Haidian District, Beijing 100193, China.
Lab3	Sun Hongfeng	China National Pesticide Quality Supervision Testing Center (Shenyang)	No.8, Shenliao East Road, Tiexi District, Shenyang City, P.R. of China

Sample information

Sample	Quantity	Batch	Declared Content of AI
Metolachlor TC-1	100 g	202106034	980 g/kg
Metolachlor TC-2	100 g	202107046	980 g/kg
Metolachlor TC-3	100 g	202108058	980 g/kg
Metolachlor EC-1	100 mL	202107048	670 g/kg
Metolachlor EC-2	100 mL	202107134	670 g/kg
Metolachlor EC-3	100 mL	202108069	670 g/kg
Metolachlor EW-1	100 mL	202106025	500 g/kg
Metolachlor EW-2	100 mL	202107042	500 g/kg
Metolachlor EW-3	100 mL	202108043	500 g/kg

3. Deviations and remarks

Lab 2 used a flow rate of 1.9 mL/m and column temperature of 181 ºC.

Column information:	HP-5, 30m×0.32mm×0.25µm	DB-5, 30m×0.32mm×0.25µm	HP-5 30m×0.32mm×0.25µm
Column Temperature (ºC):	182	181	182
Injection port temperature (ºC):	250	250	250
Detector temperature (ºC):	250	250	250
Flow rate - nitrogen (carrier), ml/min	2.0	1.9	2.0
Flow rate - hydrogen, ml/min	30	30	30
Flow rate - air, ml/min	300	300	300
Flow rate - make up, ml/min	25	25	25
Injection Volume (µL):	1.0	1	1
Split ratio	20:1	20:1	20:1

4. Statistical evaluation

Table 1. Results of the analysis of Al content in the TC-1

Lab	Day1 (g/kg)		Day2 (g/kg)		Average Yi(g/kg)	Yi^2	Standard Deviation Si	Si^2
	1	2	1	2				
Lab1	980.5	986.5	981.1	984.8	983.2	966756.0	2.9136	8.4890
Lab2	975.9	974.4	973.9	978.6	975.7	951980.7	2.1140	4.4689
Lab3	976.7	969.7	975.0	975.8	974.3	949226.4	3.1162	9.7105

Table 2. Results of the analysis of Al content in the TC-2

Lab	Day1 (g/kg)		Day2 (g/kg)		Average Yi(g/kg)	Yi^2	Standard Deviation Si	Si^2
	1	2	1	2				
Lab1	978.93	981.06	982.25	980.86	980.8	961919.6006	1.3745	1.8894
Lab2	974.47	973.85	974.11	973.57	974.0	948676.0000	0.3831	0.1468
Lab3	973.61	970.47	974.37	972.84	972.8	946383.6165	1.6881	2.8498

Table 3. Results of the analysis of Al content in the TC-3

Lab	Day1 (g/kg)		Day2 (g/kg)		Average Yi(g/kg)	Yi^2	Standard Deviation Si	Si^2
	1	2	1	2				

Lab1	980.19	981.32	981.44	984.42	981.8	964014.6948	1.8082	3.2698
Lab2	981.46	984.52	977.96	971.62	978.9	958225.6321	5.5383	30.6732
Lab3	971.68	971.21	971.23	971.86	971.5	943802.5350	0.3260	0.1063

Table 4. Results of the analysis of Al content in the EC-1

Lab	Day1 (g/kg)		Day2 (g/kg)		Average Yi(g/kg)	Yi^2	Standard Deviation Si	Si^2
	1	2	1	2				
Lab1	676.0	676.6	673.6	676.2	675.6	456428.6	1.3663	1.8668
Lab2	682.9	692.0	688.8	681.8	686.4	471086.6	4.8640	23.6582
Lab3	670.7	674.4	670.7	680.3	674.0	454269.3	4.5270	20.4936

Table 5. Results of the analysis of Al content in the EC-2

Lab	Day1 (g/kg)		Day2 (g/kg)		Average Yi(g/kg)	Yi^2	Standard Deviation Si	Si^2
	1	2	1	2				
Lab1	674.4	673.3	669.7	676.9	673.6	453676.3380	2.9920	8.9523
Lab2	686.7	681.7	687.1	683.6	684.8	468906.5291	2.5978	6.7484
Lab3	674.9	674.7	677.1	674.9	675.4	456131.3906	1.1339	1.2858

Table 6. Results of the analysis of Al content in the EC-3

Lab	Day1 (g/kg)		Day2 (g/kg)		Average Yi(g/kg)	Yi^2	Standard Deviation Si	Si^2
	1	2	1	2				
Lab1	675.9	672.5	671.0	674.6	673.5	453595.5150	2.1777	4.7424
Lab2	691.5	684.0	688.7	681.1	686.3	471059.1639	4.6623	21.7366
Lab3	674.9	679.9	678.3	680.0	678.3	460046.8016	2.4075	5.7959

Table 7. Results of the analysis of Al content in the EW-1

Lab	Day1 (g/kg)		Day2 (g/kg)		Average Yi(g/kg)	Yi^2	Standard Deviation Si	Si^2
	1	2	1	2				
Lab1	493.2	494.3	501.4	498.3	496.8	246817.6921	3.7524	14.0805
Lab2	504.3	501.8	493.8	494.6	498.6	248616.9182	5.2146	27.1923
Lab3	492.4	491.4	498.5	495.8	494.5	244542.6127	3.2874	10.8067

Table 8. Results of the analysis of Al content in the EW-2

Lab	Day1 (g/kg)	Day2 (g/kg)	Average Yi(g/kg)	Yi^2	Standard Deviation	Si^2

	1	2	1	2			Si	
Lab1	486.4	483.1	487.5	486.0	485.7	235945.7763	1.8494	3.4202
Lab2	490.3	490.7	482.8	485.7	487.4	237531.9538	3.7783	14.2755
Lab3	483.9	476.8	484.8	484.0	482.4	232690.4644	3.7367	13.9627

Table 9. Results of the analysis of Al content in the EW-3

Lab	Day1 (g/kg)		Day2 (g/kg)		Average Yi(g/kg)	Yi^2	Standard Deviation Si	Si^2
	1	2	1	2				
Lab1	492.6	494.3	494.8	494.0	493.9	243964.3753	0.9336	0.8717
Lab2	499.4	493.2	490.1	495.7	494.6	244616.7952	3.9402	15.5251
Lab3	485.9	486.2	492.3	492.0	489.1	239211.4736	3.5067	12.2966

Figure 1. Graphical presentation of TC-1 data

Figure 2. Graphical presentation of TC-2 data

Figure 3. Graphical presentation of TC-3 data

Figure 4. Graphical presentation of EC-1 data

Figure 5. Graphical presentation of EC-2 data

Figure 6. Graphical presentation of EC-3 data

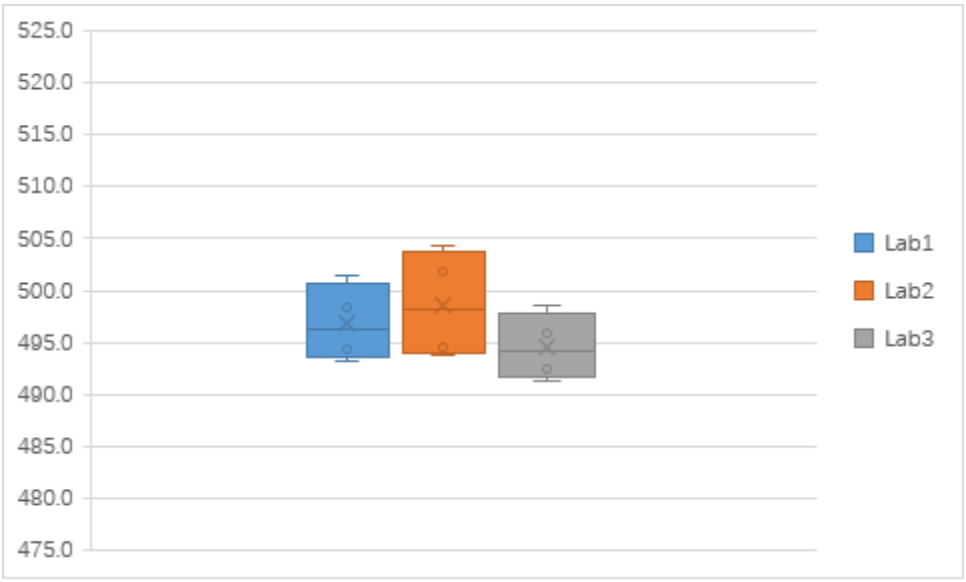

Figure 7. Graphical presentation of EW-1 data

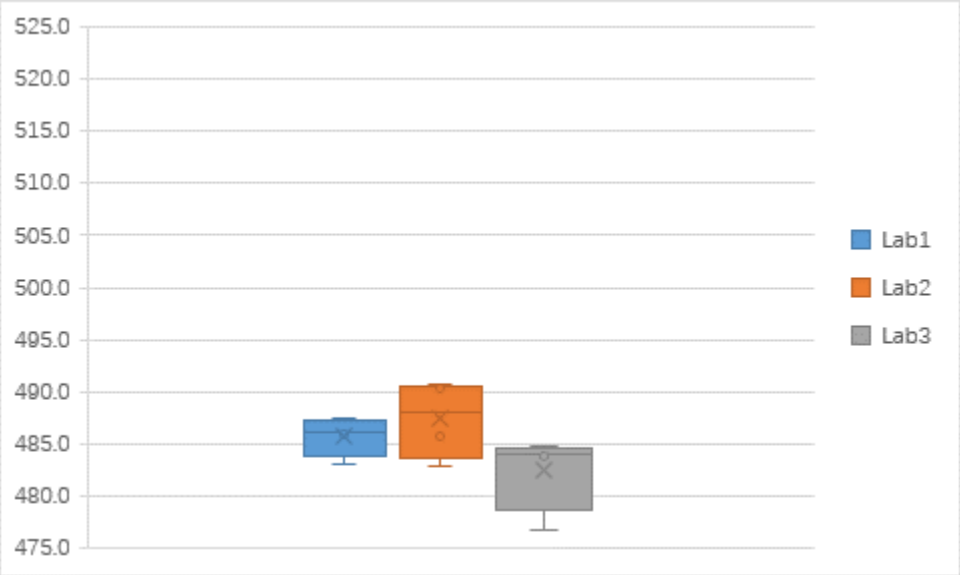

Figure 8. Graphical presentation of EW-2 data

Figure 9. Graphical presentation of EW-3 data

Table 10. Statistics of the results of TC-1

S_1=sum Yi	2933.22		
S_2=sum Yi^2	2867963.10424		
S_3=sum Si^2	22.6683		
No. Lab P	3		
No. Determination n	4		
Average Y=S_1/P	977.74		
S_r^2=S_3/P	7.5561	**Standard Deviation of Repeatability S_r**	2.7488
S_L^2=[(P*S_2-S_1^2)/P(P-1)]- S_r^2/n	21.2904	**S_L**	4.6142

$S_R^2=S_r^2+S_L^2$	28.8465	**Standard Deviation Reproducibility S_R**	5.3709
Repeatability r=2.8*Sr	7.6967		
Reproducibility R=2.8*S_R	15.0385		
Relative Standard Deviation of Repeatability $RSD_r=S_r*100/Y$	0.2811		
Relative Standard Deviation of Reproducibility $RSD_R=S_R*100/Y$	0.5493		
Horwitz RSD_R (Hor)=2^[1-0.5*log(Y/1000)]	2.0068		
HorRat	0.27372994		

Table 11. Statistics of the results of TC-2

S_1=sum Yi	2927.60		
S_2=sum Yi^2	2856979.21713		
S_3=sum Si^2	4.8860		
No. Lab P	3		
No. Determination n	4		
Average $Y=S_1/P$	975.87		
$S_r^2=S_3/P$	1.6287	**Standard Deviation of Repeatability S_r**	1.2762
$S_L^2=[(P*S_2-S_1^2)/P(P-1)]- S_r^2/n$	18.0144	**S_L**	4.2443
$S_R^2=S_r^2+S_L^2$	19.6431	**Standard Deviation Reproducibility S_R**	4.4320
Repeatability r=2.8*Sr	3.5733		
Reproducibility R=2.8*S_R	12.4097		
Relative Standard Deviation of Repeatability $RSD_r=S_r*100/Y$	0.1308		
Relative Standard Deviation of Reproducibility $RSD_R=S_R*100/Y$	0.4542		
Horwitz RSD_R (Hor)=2^[1-0.5*log(Y/1000)]	2.0074		
HorRat	0.226249456		

Table 12. Statistics of the results of TC-3

S_1=sum Yi	2932.23
S_2=sum Yi^2	2866042.86193
S_3=sum Si^2	34.0493
No. Lab P	3
No. Determination n	4

Average $Y=S_1/P$	977.41		
$S_r^2=S_3/P$	11.3498	**Standard Deviation of Repeatability S_r**	3.3689
$S_L^2=[(P*S_2-S_1^2)/P(P-1)]- S_r^2/n$	25.5749	**S_L**	5.0572
$S_R^2=S_r^2+S_L^2$	36.9247	**Standard Deviation Reproducibility S_R**	6.0766
Repeatability r=2.8*Sr	9.4330		
Reproducibility $R=2.8*S_R$	17.0144		
Relative Standard Deviation of Repeatability $RSD_r=S_r*100/Y$	0.3447		
Relative Standard Deviation of Reproducibility $RSD_R=S_R*100/Y$	0.6217		
Horwitz RSD_R (Hor)=2^[1-0.5*log(Y/1000)]	2.0069		
HorRat	0.309783417		

Table 13. Statistics of the results of EC-1

S_1=sum Yi	2035.95		
S_2=sum Yi^2	1381784.48186		
S_3=sum Si^2	46.0186		
No. Lab P	3		
No. Determination n	4		
Average $Y=S_1/P$	678.65		
$S_r^2=S_3/P$	15.3395	**Standard Deviation of Repeatability S_r**	3.9166
$S_L^2=[(P*S_2-S_1^2)/P(P-1)]- S_r^2/n$	41.3689	**S_L**	6.4319
$S_R^2=S_r^2+S_L^2$	56.7085	**Standard Deviation Reproducibility S_R**	7.5305
Repeatability r=2.8*Sr	10.9664		
Reproducibility $R=2.8*S_R$	21.0854		
Relative Standard Deviation of Repeatability $RSD_r=S_r*100/Y$	0.5771		
Relative Standard Deviation of Reproducibility $RSD_R=S_R*100/Y$	1.1096		
Horwitz RSD_R (Hor)=2^[1-0.5*log(Y/1000)]	2.1202		
HorRat	0.52336985		

Table 14. Statistics of the results of EC-2

S_1=sum Yi	2033.70		
S_2=sum Yi^2	1378714.25771		
S_3=sum Si^2	16.9865		
No. Lab P	3		
No. Determination n	4		
Average Y=S_1/P	677.90		
S_r^2=S_3/P	5.6622	**Standard Deviation of Repeatability S_r**	2.3795
S_L^2=[(P*S_2-S_1^2)/P(P-1)]- S_r^2/n	34.7931	**S_L**	5.8986
S_R^2=S_r^2+S_L^2	40.4552	**Standard Deviation Reproducibility S_R**	6.3604
Repeatability r=2.8*Sr	6.6627		
Reproducibility R=2.8*S_R	17.8092		
Relative Standard Deviation of Repeatability RSD_r=S_r*100/Y	0.3510		
Relative Standard Deviation of Reproducibility RSD_R=S_R*100/Y	0.9383		
Horwitz RSD_R (Hor)=2^[1-0.5*log(Y/1000)]	2.1205		
HorRat	0.442466128		

Table 15. Statistics of the results of EC-3

S_1=sum Yi	2038.10		
S_2=sum Yi^2	1384701.48049		
S_3=sum Si^2	32.2749		
No. Lab P	3		
No. Determination n	4		
Average Y=S_1/P	679.37		
S_r^2=S_3/P	10.7583	**Standard Deviation of Repeatability S_r**	3.2800
S_L^2=[(P*S_2-S_1^2)/P(P-1)]- S_r^2/n	39.4490	**S_L**	6.2808
S_R^2=S_r^2+S_L^2	50.2073	**Standard Deviation Reproducibility S_R**	7.0857
Repeatability r=2.8*Sr	9.1840		
Reproducibility R=2.8*S_R	19.8400		
Relative Standard Deviation of Repeatability RSD_r=S_r*100/Y	0.4828		

Relative Standard Deviation of Reproducibility $RSD_R=S_R*100/Y$	1.0430
Horwitz RSD_R (Hor)=2^[1-0.5*log(Y/1000)]	2.1198
HorRat	0.492015105

Table 16. Statistics of the results of EW-1

S_1=sum Yi	1489.94		
S_2=sum Yi^2	739977.22294		
S_3=sum Si^2	52.0795		
No. Lab P	3		
No. Determination n	4		
Average $Y=S_1/P$	496.65		
$S_r^2=S_3/P$	17.3598	**Standard Deviation of Repeatability S_r**	4.1665
$S_L^2=[(P*S_2-S_1^2)/P(P-1)]- S_r^2/n$	0.1125	**S_L**	0.3354
$S_R^2=S_r^2+S_L^2$	17.4724	**Standard Deviation Reproducibility S_R**	4.1800
Repeatability r=2.8*Sr	11.6662		
Reproducibility $R=2.8*S_R$	11.7040		
Relative Standard Deviation of Repeatability $RSD_r=S_r*100/Y$	0.8389		
Relative Standard Deviation of Reproducibility $RSD_R=S_R*100/Y$	0.8416		
Horwitz RSD_R (Hor)=2^[1-0.5*log(Y/1000)]	2.2222		
HorRat	0.378747709		

Table 17. Statistics of the results of EW-2

S_1=sum Yi	1455.50		
S_2=sum Yi^2	706168.19446		
S_3=sum Si^2	31.6584		
No. Lab P	3		
No. Determination n	4		
Average $Y=S_1/P$	485.17		
$S_r^2=S_3/P$	10.5528	**Standard Deviation of Repeatability S_r**	3.2485
$S_L^2=[(P*S_2-S_1^2)/P(P-1)]- S_r^2/n$	3.8432	**S_L**	1.9604

$S_R^2=S_r^2+S_L^2$	14.3960	**Standard Deviation Reproducibility S_R**	3.7942
Repeatability r=2.8*Sr	9.0958		
Reproducibility R=2.8*S_R	10.6238		
Relative Standard Deviation of Repeatability $RSD_r=S_r*100/Y$	0.6696		
Relative Standard Deviation of Reproducibility $RSD_R=S_R*100/Y$	0.7820		
Horwitz RSD_R (Hor)=2^[1-0.5*log(Y/1000)]	2.2300		
HorRat	0.350689859		

Table 18. Statistics of the results of EW-3

S_1=sum Yi	1477.61		
S_2=sum Yi^2	727792.64397		
S_3=sum Si^2	28.6934		
No. Lab P	3		
No. Determination n	4		
Average $Y=S_1/P$	492.54		
$S_r^2=S_3/P$	9.5645	**Standard Deviation of Repeatability S_r**	3.0926
$S_L^2=[(P*S_2-S_1^2)/P(P-1)]- S_r^2/n$	6.6102	**S_L**	2.5710
$S_R^2=S_r^2+S_L^2$	16.1747	**Standard Deviation Reproducibility S_R**	4.0218
Repeatability r=2.8*Sr	8.6594		
Reproducibility R=2.8*S_R	11.2610		
Relative Standard Deviation of Repeatability $RSD_r=S_r*100/Y$	0.6279		
Relative Standard Deviation of Reproducibility $RSD_R=S_R*100/Y$	0.8165		
Horwitz RSD_R (Hor)=2^[1-0.5*log(Y/1000)]	2.2250		
HorRat	0.366992373		

A Grubbs test were run on all determinations, and no outlier was found.

5. Conclusion

No outlier was found in the data set.

All RSD_R values were lower than the criteria calculated using the Horwitz equation. All HorRat values were smaller than 1.0, while 2 values fell below 0.3.

From the results shown above, the method can be considered applicable for the determination of metolachlor contents in TC, EC and EW. CHIPAC propose that a full scale collaborative trial might be conducted.

6. Figures

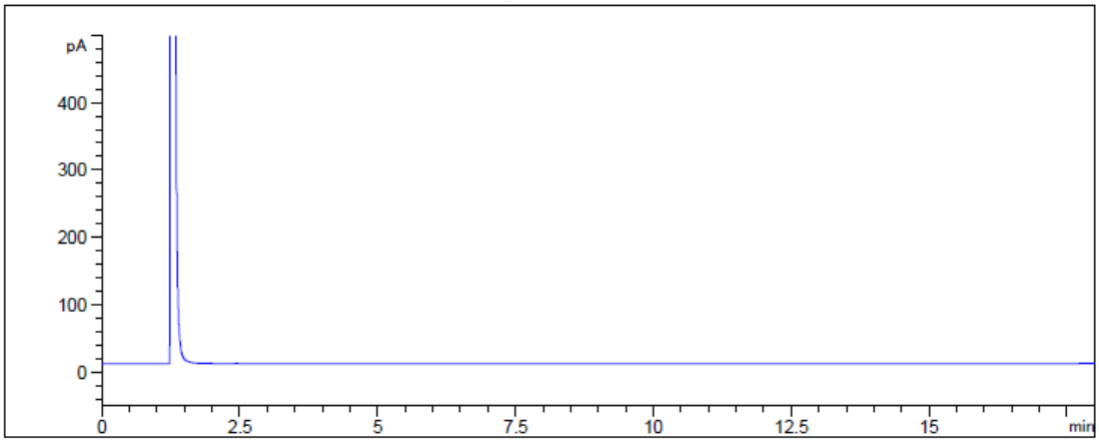

Fig.1 GC chromatogram of solvent blank

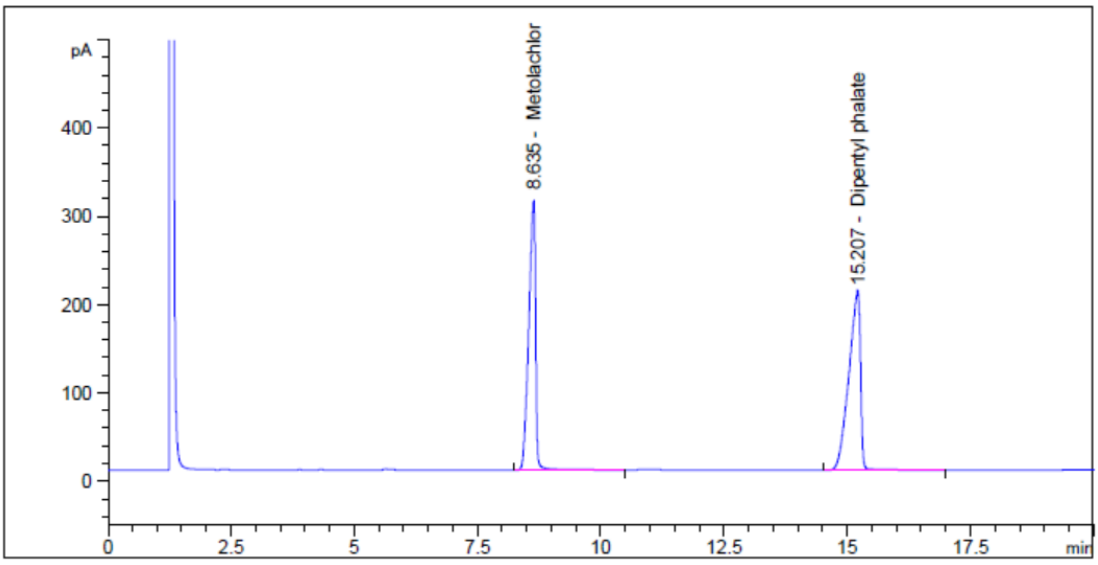

Fig.2 GC chromatogram of Metolachlor standard

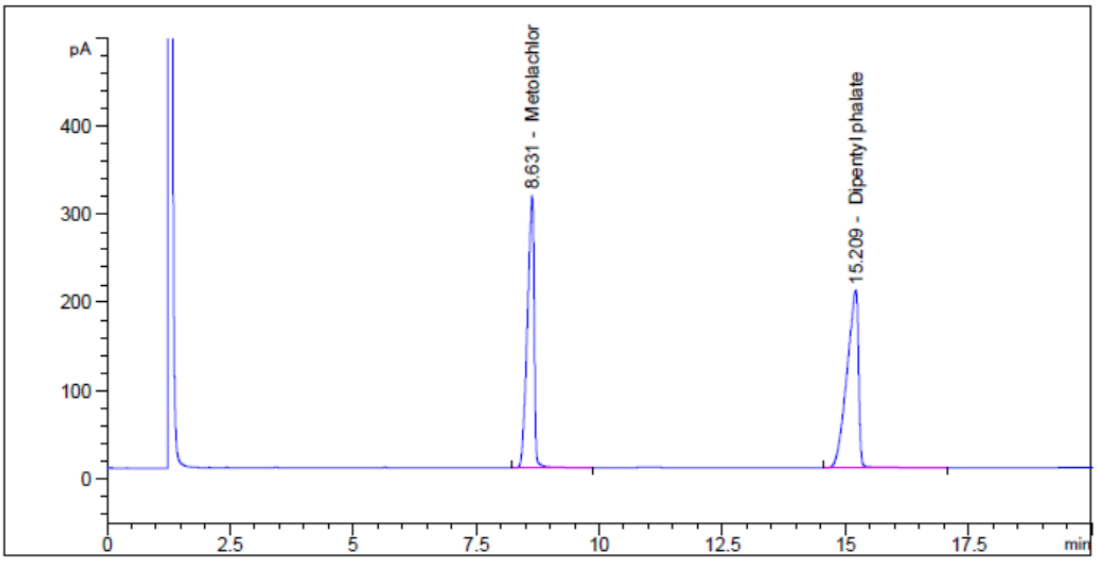

Fig.3 GC chromatogram of Metolachlor TC

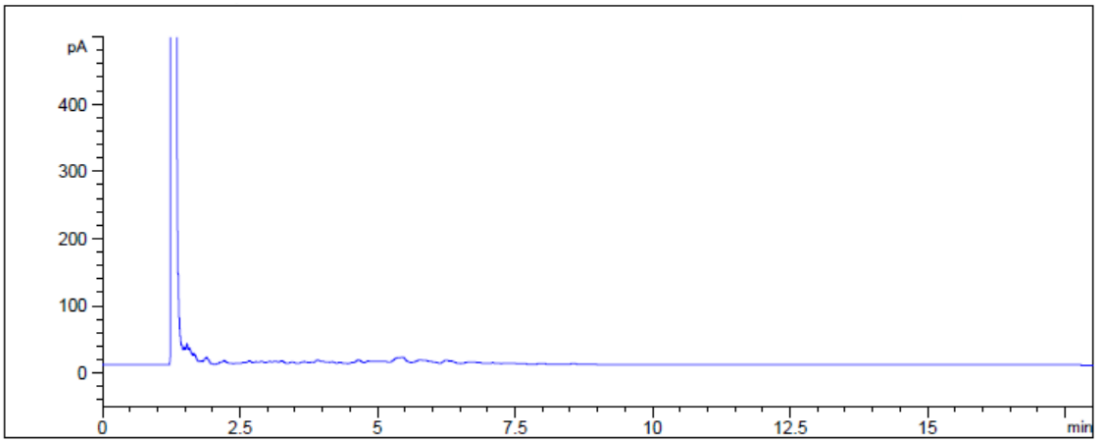

Fig.4 GC chromatogram of Metolachlor EC blank

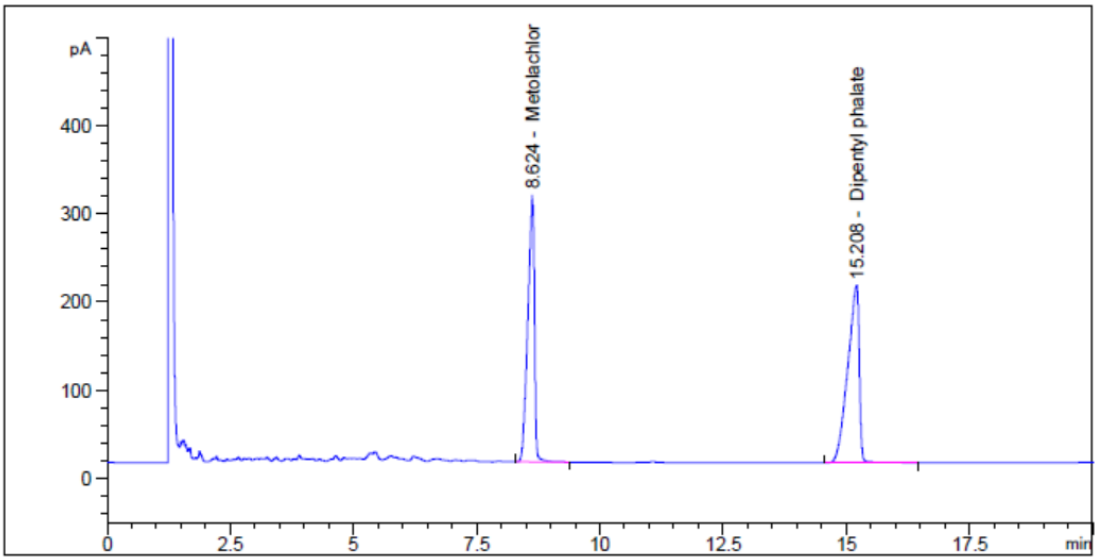

Fig.5 GC chromatogram of Metolachlor EC

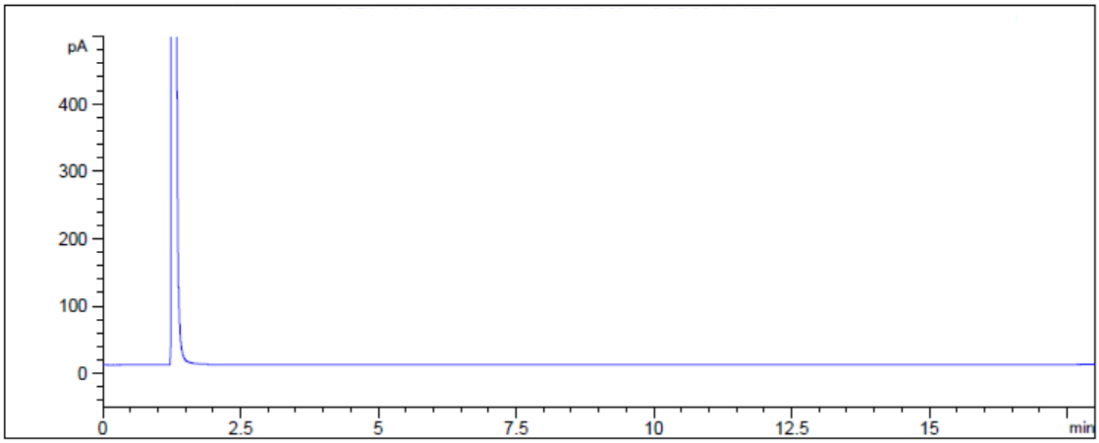

Fig.6 GC chromatogram of Metolachlor EW blank

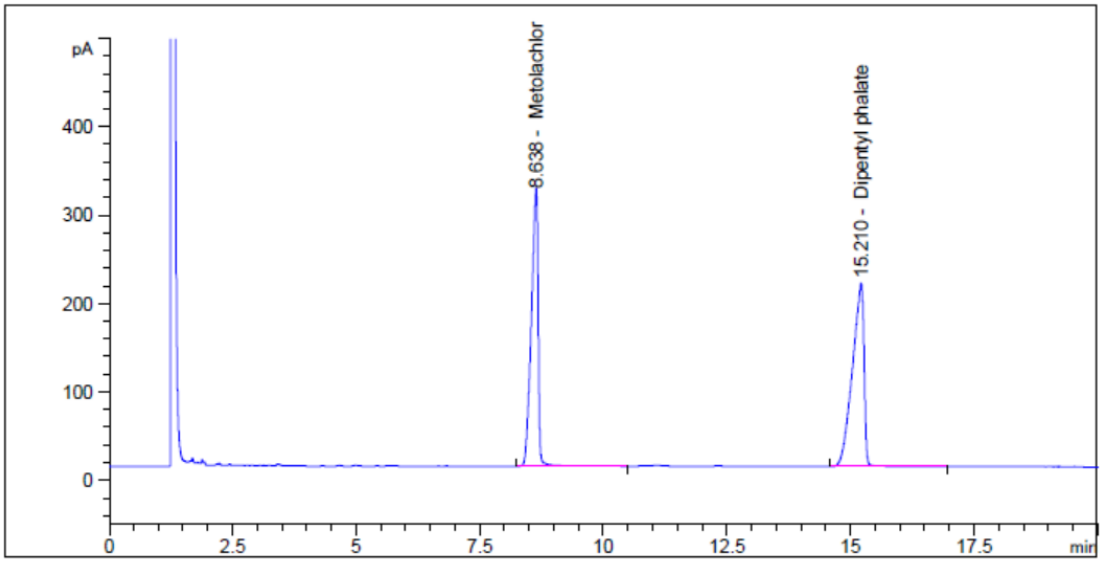

Fig.7 GC chromatogram of Metolachlor EW