METOLACHLOR

Collaborative Study

Full Scale Collaborative Study for the Determination of Metolachlor in TC, EC and EW by GC

Report to CIPAC by CHIPAC

Method Developed by
Shandong Binnong Technology Co., Ltd

May 2023

Content

1. Participants

In February 2023, Information Sheet No. 339 was sent out by the CIPAC Secretary inviting members to participate in a collaborative study on the determination of metolachlor as a technical material and in formulations.

By mid of May 2023, all participants (19 laboratorys) with the exception of one laboratory (due to the problem of sample receiving) provided their results.

The results for the 18 participants are presented in the following section.

Participating laboratories are listed in the table below.

Elen Karasali, Petros Tsiantas, Anna Marousopoulou	Benaki Phytopathological Institute. 8 Stefanou Delta Street, Kifissia, Athens, 14561 Greece.
Olga Novakova	UKZUZ (Central Institute for Supervising and Testing in Agriculture). Zemedelska 1a, 61300 Brno Czech Republic.
Pierre Hucorne	Walloon Agricultural Research Centre (CRA-W) Knowledge and Valorization of Products Department (D4) Protection, control products and residues Unit (U10) Building Rachel Carson Rue du Bordia, 115030 Gembloux Belgique
Wendy Wang	Jiangsu Agrochem Laboratory Co., Ltd. No.98, Minjiang Road, Hi-Tech Development Zone, Changzhou, P. R. China.
Yily Yan	Jiangsu Rotam Chemistry Co., Ltd. 233 Songjiagang Road, Zhoushi Town, Kunshan, P. R. China.
Aiping Xu	Laprode (Zhejiang) analysis Co., Ltd. 4/F, Building 6, No.503 Xingguo Road, Yuhang District, Hangzhou, P.R. China.
Peng Shen	JiangSu EverTest Co., Ltd. No. 31-1, Hengjing St., Economic and Technological Development Zone, Nanjing, P. R. China.
Aysel TAKKABULAN	Republic of Turkiye Ministry of Agriculture and Forestry Directorate of Plant Protection Central Research Institute. Gayret Mah. Fatih Sultan Mehmet Bul. No:66 Yenimahalle, Ankara, TURKIYE.
Christian Mink	Syngenta Crop Protection AG. Breitenloh 5, 4333 Münchwilen, Switzerland.
Yao Chen	Pilarcise Laboratory Co., Ltd. 2# Building .1500 Hang-Tang Road,Feng Xian District, Shanghai, P. R. China.
Cornel Grecu	Biochem SRL. Complexului no. 7 street, Dragalina 917080, Calarasi District, Romania

Wenzhuo Wang	Institute for the Control of Agrochemicals, Ministry of Agricultrue and Rural Affairs. Maizidian street 22, Chaoyang District, Beijing, P. R. China.
Zhiyu He	Guizhou Jiandee Technology Co., LTD. Baijin road No.3491,Baiyun district, Guiyang, P. R. China.
Chaohong He	National Testing & Certification International Group Jingcheng Testing Co., Ltd. No.201, Yiheng West Road, Donghuan Street, Panyu District, Guangzhou,P. R. China.
Lu Huang	Hunan Research Institute of Chemical Industry Testing Technology Co., Ltd. No.550, Changsha Avenue,Yuhua district, Changsha, P. R. China.
Jianwei Lv	Shanghai Lvze Biotechnology Co., Ltd. No. 200,HuaJia Road, SongJiang District ShangHai 201611,P.R. China.
Haixia Wang	Shenyang SYRICI Testing Co., Ltd. No.8, Shenliao East Road, Tiexi District Shenyang 110021, P.R. China.
Judy Dong	Shandong Binnong Technology Co., Ltd. No.518, Yongxin Road, Binbei Town, Binzhou, P.R. China
Tom Phillips, Gyan Aryal	Maryland Department of Agriculture State Chemist Section, Maryland Department of Agriculture, 50 Harry S Truman Parkway, Annapolis MD 21401, USA

2. Metolachlor, General Information

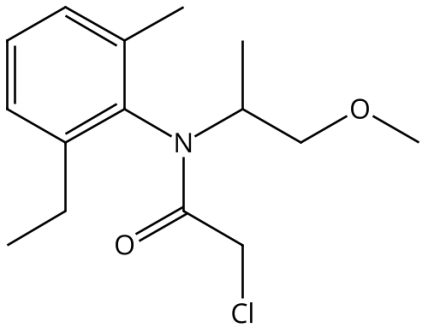
Chemical name: 2-chloro-6′-ethyl-N-(2-methoxy-1-methylethyl)acet-o-toluidine (IUPAC);

2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)-acetamide

Common name: Metolachlor

CAS-Number: 51218-45-2

Structure:



Molecular mass: 283.8 g/mol

Empirical formula: $C_{15}H_{22}ClNO_2$

3. Samples

Eight test samples (described below), including the Metolachlor analytical reference standard were shipped to the participants:

A) Metolachlor TC-1
B) Metolachlor TC-2
C) Metolachlor EC-1
D) Metolachlor EC-2
E) Metolachlor EC-3
F) Metolachlor EW-1
G) Metolachlor EW-2
H) Metolachlor EW-3

Metolachlor analytical reference standard (99.3% purity)

4. Method

4.1 Scope

The contents of Metolachlor in technical materials and in formulated products (emulsifiable concentrates; emulsions, oil in water) were determined.

4.2 Principle

The content of Metolachlor in the technical materials and the formulation (EC, EW) is determined by capillary gas chromatography on a HP-5 or equivalent fused silica column, 30 m x 0.32 mm (i.d.), 0.25 μm film thickness using nitrogen carrier gas and flame ionization detection. Quantification is done by internal standard calibration.

4.3 Procedure

Samples should be analyzed in duplicate at two different days resulting in a total of four individual test results for each sample. All test solutions should be prepared freshly on Day 2.

5. Remarks of the Participants

Participants made comments about the performance of the method and noted deviations from the method. Below is a summary of specific method conditions provided by the participating laboratories.

Lab Number	GC-System	Injection volume，μl	Column Temperature	Injection port temperature，℃	Detector Temperature，℃	Column	Gas of Flow rate and detector mL/min	Split ratio	Remarks
Laboratory 1	Agilent 7890A	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier, He); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 2	Agilent 7890B	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier, He); 30(hydrogen); 300(air); 25(make up)	30：1	.
Laboratory 3	Agilent 7890B	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 4	Agilent 6890B	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.25 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	In this method, the retention time of principal component and internal standard were both in the process of programmed heating.

Laboratory 5	Thermo TRACE 1300	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	TG-5MS, 30m×0.32mm×0.25μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 6	SHIMADZU GC-2010 PLUS	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 7	Agilent 7890A	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 8	Agilent 8860	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 9	Agilent 6890N	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	* split ratio 30:1 - high fronting peaks (peak symmetry > 2)
Laboratory 10	Shimadzu GC-2010 Plus	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 11	THERMO TRACE 1610	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	TG-5 SILMS, 30×0.32 mm×0.25 μm	2.0 (carrier); 35(hydrogen); 350(air); 40(make up)	30：1	

Laboratory 12	Agilent 7890A	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 13	Agilent 8890	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 14	Agilent 6890N	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	Agilent J&V DB-5 MS capillary, 30×0.25 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	Helium was used as carrier gas in the Agilent 6890 device. Retention time for metolachlor: about 6.8 min and for internal standard: about 9.2 min. The simplicity of the sample preparation process and less solvent consumption were the outstanding features of the method.
Laboratory 15	Agilent 7890	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier,He); 30(hydrogen); 300(air); 25(make up)	30：1	Deviation: we used helium instead of nitrogen as the carrier gas, because we don't use nitrogen typically.
Laboratory 16	Agilent 6890N	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	HP-5, 30×0.32 mm×0.25 μm	2.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	

Laboratory 17	Shimadzu GC-2010 Plus	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	250	RTX-5, 30×0.25 mm×0.25 μm	1.0 (carrier); 30(hydrogen); 300(air); 25(make up)	30：1	
Laboratory 18	Shimadzu GC-2010 Plus	1.0	initially set to 180℃ which keep for 1min, then increased to 230 ℃ at 5 ℃/min, and remain for 1 min	250	300	DB-5, 30×0.5 mm×1.5 μm	6.7 (carrier); 40(hydrogen); 400(air); 30(make up)	30：1	

6. Evaluation and Discussion

6.1 Evaluation of the Quality of Data and Chromatograms

The data obtained from each of the laboratories were reviewed to determine if there were any significant deviations regarding the chromatography which might affect the analysis results.
Visual examination of the chromatograms showed no evidence for invalid data.
All other changes and observations noted by the 18 participants were not expected to affect the analysis results significantly.

6.2 Determination of Metolachlor

Results reported by the laboratories and the statistical evaluation are listed in tables 1-10 and displayed in figures 1-8.

The statistical evaluation of the data was done following the “Guidelines for CIPAC Collaborative Study Procedures for Assessment of Performance of Analytical Methods”, according to DIN ISO 5725. The data were examined for outliers and stragglers using the Grubbs test, and iterating where necessary. The tests were performed at an alpha level of 0.01 for outlier (marked with **), and 0.05 for straggler (marked with *).

A comparison of the RSD_R of this collaborative study with the unmodified Horwitz equation showed that the reproducibility relative standard deviation (RSD_R) is below the Horwitz value in all samples (TC-1, TC-2, EC-1, EC-2, EC-3, EW-1, EW-2 and EW-3) even without elimination of stragglers and outliers (see Table 10). All HorRat values were smaller than 1.0, while the TC2’s result fell below 0.3. Due to the universal applicability of the method this collaborative trial is acceptable.

Table 1 Results of analysis of metolachlor content in the TC1

	Day1(g/kg)		Day2(g/kg)		Average Yi	Standard Deviation S_i
	1	2	1	2		
Lab 1	977.9	981.4	981.1	985.2	981.4	2.988
Lab 2	986.5	985.3	980.7	982.4	983.7	2.651
Lab 3	989.6	987.2	983.9	984.3	986.3	2.674
Lab 4	985.8	987.3	986.3	986.8	986.6	0.6455
Lab 5	1002.0	989.1	992.1	983.1	991.6	7.893
Lab 6	983.2	982.9	982.4	983.1	982.9	0.3559
Lab 7	984.1	985.7	986.8	985.6	985.6	1.109
Lab 8	986.3	981.2	991.3	993.7	988.1	5.551
Lab 9	991.4	994.8	986.0	984.9	989.3	4.651
Lab 10	979.0	981.9	979.8	982.7	980.9	1.737
Lab 11	991.3	989.9	990.0	996.8	992.0	3.263
Lab 12	982.3	987.5	988.6	986.0	986.1	2.748
Lab 13	978.0	978.8	977.6	977.7	978.0	0.5439
Lab 14	982.1	982.8	989.9	988.9	985.9	4.043
Lab 15	986.6	983.6	985.6	984.2	985.0	1.356
Lab 16	983.4	985.8	982.0	984.5	983.9	1.615
Lab 17	976.0	978.4	977.8	978.3	977.6	1.115
Lab 18	991.0	990.8	992.6	990.4	991.2	0.9661

Table 2 Results of analysis of metolachlor content in the TC2

	Day1(g/kg)		Day2(g/kg)		Average Yi	Standard Deviation S_i
	1	2	1	2		
Lab 1	973.0	974.6	978.0	983.3	977.2	4.555
Lab 2	976.4	983.3	995.7	984.1	984.9	8.002
Lab 3	988.0	986.9	986.5	985.4	986.7	1.074
Lab 4	987.4	988.2	984.8	987.1	986.9	1.459
Lab 5	986.0	990.6	978.5	983.5	984.7	5.045
Lab 6	982.4	982.3	981.5	981.7	982.0	0.443
Lab 7	982.9	979.6	984.6	983.8	982.7	2.196
Lab 8	974.4	981.2	985.9	985.6	981.8	5.366
Lab 9	996.3	986.6	976.3	984.5	985.9	8.221
Lab 10	978.9	982.7	982.1	980.4	981.0	1.719
Lab 11	985.8	984.2	987.5	983.8	985.3	1.688
Lab 12	986.1	986.6	988.0	986.9	986.9	0.804
Lab 13	978.9	978.7	981.8	978.5	979.5	1.559
Lab 14	981.3	979.6	988.5	985.7	983.8	4.066
Lab 15	982.3	986.2	985.5	983.3	984.3	1.830

Lab 16	984.3	985.0	984.4	984.2	984.5	0.359
Lab 17	981.9	977.5	977.6	977.0	978.5	2.282
Lab 18	986.6	984.8	987.2	984.1	985.7	1.464

Table 3 Results of analysis of metolachlor content in the EC1

	Day1(g/kg)		Day2(g/kg)		Average Yi	Standard Deviation S_i
	1	2	1	2		
Lab 1	695.4	695.0	695.9	696.9	695.8	0.821
Lab 2	703.4	696.8	698.2	701.2	699.9	2.969
Lab 3	702.1	704.6	696.8	701.6	701.3	3.259
Lab 4	697.5	701.4	698.0	700.1	699.3	1.823
Lab 5	699.5	685.9	690.1	691.9	691.9	5.686
Lab 6	696.2	695.4	697.1	697.2	696.5	0.846
Lab 7	696.0	696.0	703.7	697.3	698.3	3.685
Lab 8	702.7	703.8	709.4	705.0	705.2	2.938
Lab 9	705.0	699.6	697.7	700.4	700.7	3.098
Lab 10	691.7	692.8	693.3	694.6	693.1	1.203
Lab 11	699.2	699.6	701.2	700.7	700.2	0.932
Lab 12	695.4	695.9	699.4	697.5	697.1	1.805
Lab 13	687.4	689.2	689.4	689.8	689.0	1.063
Lab 14	693.1	695.5	698.9	699.5	696.8	3.004
Lab 15	694.2	697.2	695.6	696.7	695.9	1.330
Lab 16	695.3	696.3	696.3	694.0	695.5	1.090
Lab 17	689.4	691.8	690.1	694.3	691.4	2.180
Lab 18	693.9	691.0	700.3	703.1	697.1	5.588

Table 4 Results of analysis of metolachlor content in the EC2

	Day1(g/kg)		Day2(g/kg)		Average Yi	Standard Deviation S_i
	1	2	1	2		
Lab 1	693.3	695.2	696.3	696.9	695.4	1.582
Lab 2	694.3	697.8	699.2	700.7	698.0	2.736
Lab 3	699.7	700.5	704.1	699.4	700.9	2.167
Lab 4	697.1	697.6	696.9	697.5	697.3	0.330
Lab 5	698.1	695.9	691.8	688.7	693.6	4.195
Lab 6	693.2	694.2	694.3	694.8	694.1	0.670
Lab 7	700.4	699.0	697.5	697.1	698.5	1.508
Lab 8	700.1	700.1	706.7	702.9	702.5	3.126
Lab 9	700.8	704.0	696.7	698.4	700.0	3.167
Lab 10	693.1	692.3	693.8	695.0	693.6	1.145
Lab 11	696.3	697.1	696.3	698.8	697.1	1.179
Lab 12	697.0	694.5	697.6	699.0	697.0	1.880

Lab 13	687.0	689.1	686.2	685.9	687.1	1.443
Lab 14	695.0	699.4	700.3	706.0	700.2	4.521
Lab 15	695.3	693.1	697.1	695.2	695.2	1.636
Lab 16	694.2	695.0	694.9	694.3	694.6	0.408
Lab 17	695.7	697.0	695.7	695.0	695.9	0.835
Lab 18	692.4	689.3	709.1	708.0	699.7	10.31

Table 5 Results of analysis of metolachlor content in the EC3

	Day1(g/kg)		Day2(g/kg)		Average Yi	Standard Deviation S_i
	1	2	1	2		
Lab 1	692.1	696.6	693.6	693.8	694.0	1.877
Lab 2	693.0	692.3	698.9	703.1	696.8	5.125
Lab 3	705.8	703.5	699.4	699.9	702.2	3.042
Lab 4	700.0	702.5	698.3	699.0	700.0	1.838
Lab 5	704.6	700.9	674.8	686.9	691.8	13.66
Lab 6	696.1	695.4	696.1	697.9	696.4	1.069
Lab 7	698.5	697.9	699.5	696.8	698.2	1.130
Lab 8	701.0	699.6	707.2	698.7	701.6	3.835
Lab 9	701.0	702.7	698.1	696.2	699.5	2.906
Lab 10	695.4	693.9	694.1	695.2	694.7	0.759
Lab 11	699.2	698.5	696.1	700.6	698.6	1.881
Lab 12	696.9	697.6	698.1	699.6	698.1	1.145
Lab 13	686.6	688.8	691.1	689.4	689.0	1.859
Lab 14	701.7	693.1	700.9	700.0	698.9	3.945
Lab 15	697.7	695.8	695.0	696.7	696.3	1.163
Lab 16	697.7	696.5	695.3	695.0	696.1	1.234
Lab 17	697.3	698.6	694.0	694.5	696.1	2.211
Lab 18	689.3	690.5	710.0	705.6	698.9	10.50

Table 6 Results of analysis of metolachlor content in the EW1

	Day1(g/kg)		Day2(g/kg)		Average Yi	Standard Deviation S_i
	1	2	1	2		
Lab 1	502.7	502.1	497.4	494.3	499.1	3.995
Lab 2	505.3	507.0	507.8	509.2	507.3	1.628
Lab 3	506.0	508.2	507.5	508.2	507.5	1.037
Lab 4	507.5	507.5	506.4	506.2	506.9	0.698
Lab 5	499.9	490.2	490.6	489.0	492.4	5.029
Lab 6	506.9	505.3	507.2	505.4	506.2	0.990
Lab 7	511.4	508.1	507.6	508.5	508.9	1.707
Lab 8	507.3	506.8	512.4	511.2	509.4	2.793
Lab 9	512.3	510.3	507.4	506.2	509.1	2.767

Lab 10	501.2	500.1	499.4	502.5	500.8	1.354
Lab 11	508.4	504.2	509.1	507.7	507.4	2.176
Lab 12	506.0	506.6	507.1	508.8	507.1	1.204
Lab 13	497.4	497.2	498.8	497.6	497.8	0.719
Lab 14	507.0	507.2	510.5	509.2	508.5	1.676
Lab 15	507.3	505.8	508.3	505.9	506.8	1.198
Lab 16	503.0	502.6	502.1	504.6	503.1	1.081
Lab 17	504.0	501.4	501.4	505.0	503.0	1.836
Lab 18	494.3	501.5	507.9	506.1	502.5	6.065

Table 7 Results of analysis of metolachlor content in the EW2

	Day1(g/kg)		Day2(g/kg)		Average Yi	Standard Deviation S_i
	1	2	1	2		
Lab 1	483.3	484.0	487.0	484.1	484.6	1.639
Lab 2	505.8	508.1	511.4	507.4	508.2	2.356
Lab 3	506.5	506.1	500.5	501.1	503.6	3.189
Lab 4	506.5	510.7	508.3	509.2	508.7	1.756
Lab 5	491.0	483.9	479.0	469.9	481.0	8.862
Lab 6	502.4	502.3	502.9	501.4	502.3	0.624
Lab 7	510.6	507.3	508.2	508.7	508.7	1.393
Lab 8	508.1	507.4	512.9	511.9	510.1	2.731
Lab 9	510.1	509.6	506.5	506.0	508.1	2.098
Lab 10	499.5	500.7	502.9	504.3	501.9	2.156
Lab 11	506.7	507.4	508.4	507.4	507.5	0.699
Lab 12	509.1	506.4	510.6	509.2	508.8	1.756
Lab 13	496.2	500.3	499.2	497.3	498.3	1.845
Lab 14	507.9	506.5	506.3	509.5	507.6	1.482
Lab 15	504.5	509.0	507.9	508.4	507.5	2.017
Lab 16	503.0	503.5	504.8	503.1	503.6	0.829
Lab 17	504.9	504.6	503.2	505.9	504.7	1.115
Lab 18	500.1	501.3	510.7	511.7	506.0	6.096

Table 8 Results of analysis of metolachlor content in the EW3

	Day1(g/kg)		Day2(g/kg)		Average Yi	Standard Deviation S_i
	1	2	1	2		
Lab 1	491.8	488.2	490.9	485.0	489.0	3.060
Lab 2	502.0	501.8	505.8	506.4	504.0	2.439
Lab 3	504.6	505.8	506.4	505.0	505.5	0.806
Lab 4	504.2	505.2	504.6	505.3	504.8	0.519
Lab 5	489.0	498.1	486.5	490.7	491.1	4.991
Lab 6	501.4	501.1	502.8	503.2	502.1	1.031
Lab 7	505.1	507.9	506.4	508.1	506.9	1.406

Lab 8	487.4	487.2	490.0	495.8	490.1	4.008
Lab 9	509.4	510.4	504.9	502.0	506.7	3.929
Lab 10	501.1	501.8	504.3	503.9	502.8	1.565
Lab 11	502.5	501.7	506.3	505.4	504.0	2.220
Lab 12	503.7	504.5	505.4	506.2	505.0	1.085
Lab 13	496.9	502.5	497.2	500.3	499.2	2.670
Lab 14	503.8	502.2	505.4	505.9	504.3	1.676
Lab 15	504.1	504.7	504.2	504.2	504.3	0.271
Lab 16	504.8	501.5	504.9	503.6	503.7	1.581
Lab 17	503.4	500.0	504.6	505.0	503.3	2.271
Lab 18	505.0	505.1	511.1	509.5	507.7	3.101

Table 9 Mean values

	Metolachlor TC-1	Metolachlor TC-2	Metolachlor EC-1	Metolachlor EC-2	Metolachlor EC-3	Metolachlor EW-1	Metolachlor EW-2	Metolachlor EW-3
Lab 1	981.4	977.2	695.8	695.4	694.0	499.1	484.6**	489.0
Lab 2	983.7	984.9	699.9	698.0	696.8	507.3	508.2	504.0
Lab 3	986.3	986.7	701.3	700.9	702.2	507.5	503.6	505.5
Lab 4	986.6	986.9	699.3	697.3	700.0	506.9	508.7	504.8
Lab 5	991.6	984.7	691.9	693.6	691.8	492.4*	481.0*	491.1
Lab 6	982.9	982.0	696.5	694.1	696.4	506.2	502.3	502.1
Lab 7	985.6	982.7	698.3	698.5	698.2	508.9	508.7	506.9
Lab 8	988.1	981.8	705.2	702.5	701.6	509.4	510.1	490.1
Lab 9	989.3	985.9	700.7	700.0	699.5	509.1	508.1	506.7
Lab 10	980.9	981.0	693.1	693.6	694.7	500.8	501.9	502.8
Lab 11	990.7	985.3	700.2	697.1	698.6	507.4	507.5	504.0
Lab 12	986.1	986.9	697.1	697.0	698.1	507.1	508.8	505.0
Lab 13	978.0	979.5	689.0	687.1*	689.0	497.8	498.3	499.2
Lab 14	985.9	983.8	696.8	700.2	698.9	508.5	507.6	504.3
Lab 15	985.0	984.3	695.9	695.2	696.3	506.8	507.5	504.3
Lab 16	983.9	984.5	695.5	694.6	696.1	503.1	503.6	503.7
Lab 17	977.6	978.5	691.4	695.9	696.1	503.0	504.7	503.3
Lab 18	991.3	985.7	697.1	699.7	698.9	502.5	506.0	507.7

* Grubbs test straggler
** Grubbs test outlier

Table10 Summary of the statistical evaluation - no elimination of any outliers /stragglers

	Metolachlor TC-1	Metolachlor TC-2	Metolachlor EC-1	Metolachlor EC-2	Metolachlor EC-3	Metolachlor EW-1	Metolachlor EW-2	Metolachlor EW-3
Xm [g/kg]	985.3	983.5	696.9	696.7	697.1	504.6	503.4	501.9
L	18	18	18	18	18	18	18	18
S_r	3.198	3.735	2.818	3.278	4.696	2.570	3.084	2.489
S_R	5.052	4.356	4.658	4.560	5.227	5.159	8.546	6.170
S_L	3.911	2.240	3.709	3.170	2.295	4.473	7.970	5.646
r	8.955	10.46	7.891	9.179	13.15	7.197	8.635	6.969
R	14.15	12.20	13.04	12.77	14.64	14.45	23.93	17.28
RSD_r	0.3246	0.3798	0.4044	0.4705	0.6738	0.5093	0.6127	0.4959
RSD_R	0.52	0.44	0.67	0.65	0.75	1.02	1.70	1.23
RSD_R (Hor)	2.00	2.01	2.11	2.11	2.11	2.22	2.22	2.22
HorRat	0.3	0.2	0.3	0.3	0.4	0.5	0.8	0.6

X_m = average

L = number of laboratories

S_r = repeatability standard deviation

RSD_r = repeatability relative standard deviation

r = repeatability

S_R = reproducibility standard deviation

RSD_R = reproducibility relative standard deviation

R = reproducibility

S_L = “pure” between laboratory standard deviation

RSD_R (Hor) = Horwitz value calculated from: $2^{(1 - 0.5\log c)}$

where c = the concentration of the analyte as a decimal fraction

Figures 1 – 8 (all results)

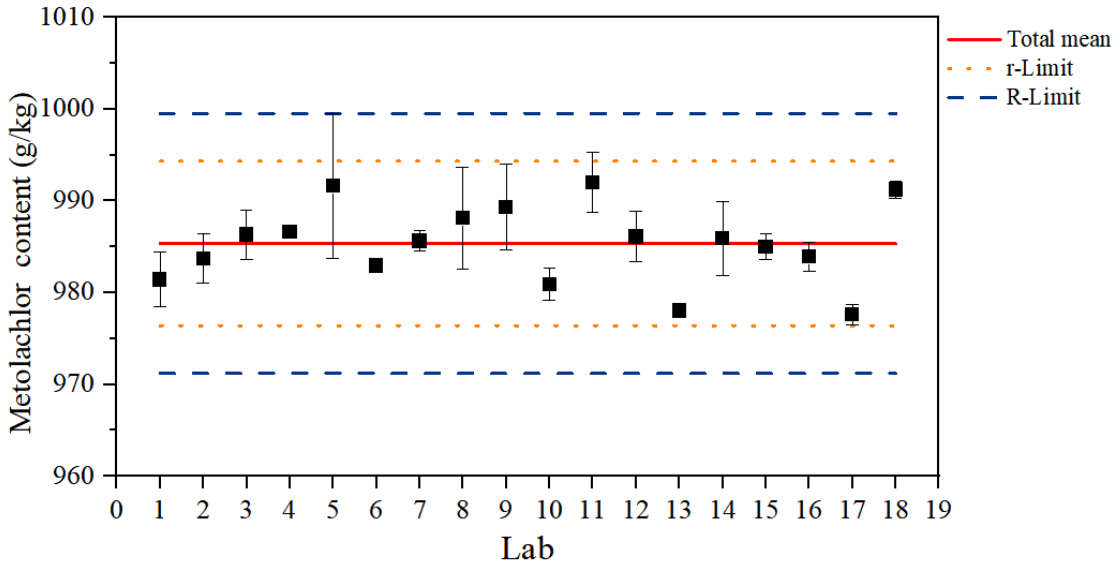


Figure 1. Graphical presentation of TC1 data

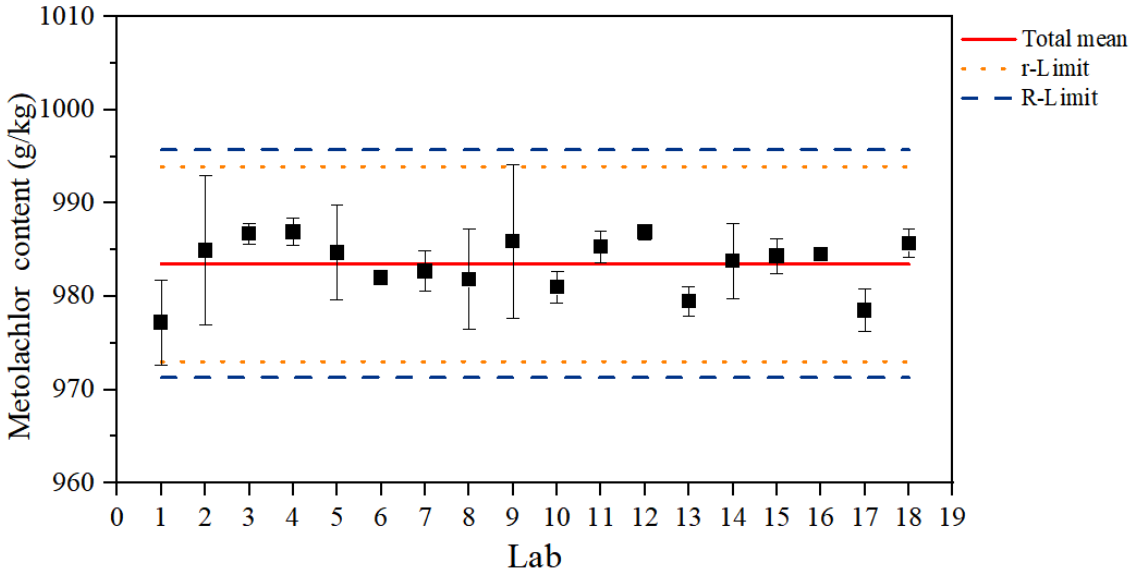


Figure 2. Graphical presentation of TC2 data

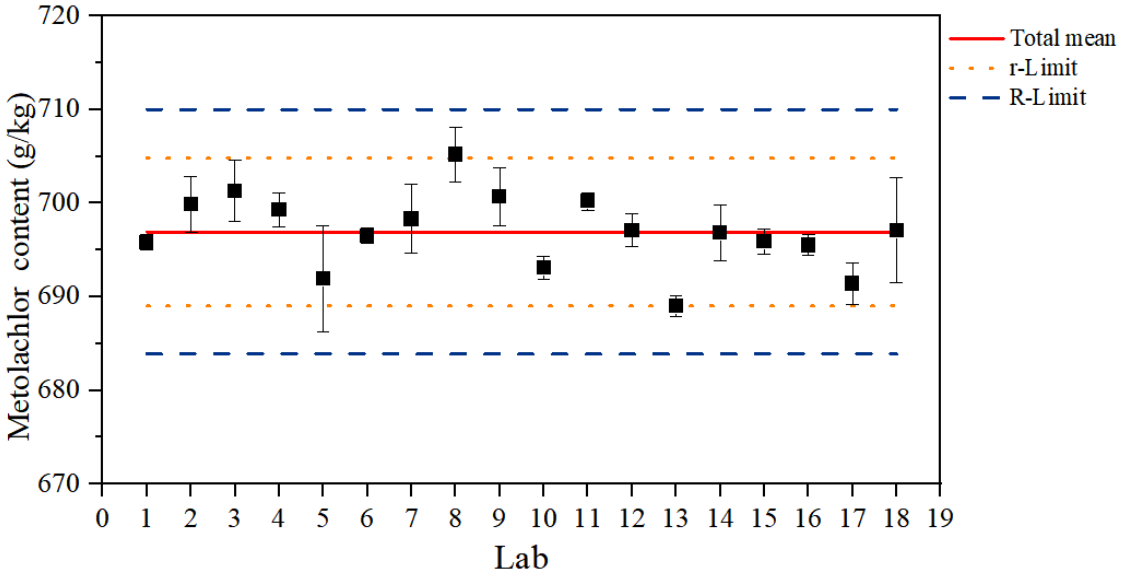


Figure 3. Graphical presentation of EC1 data

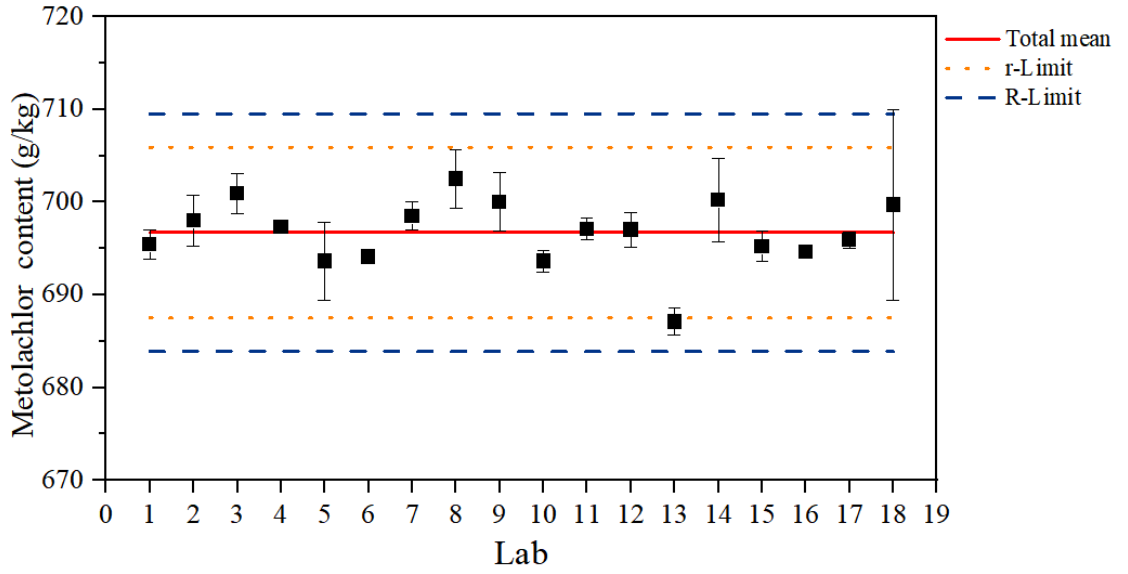


Figure 4. Graphical presentation of EC2 data

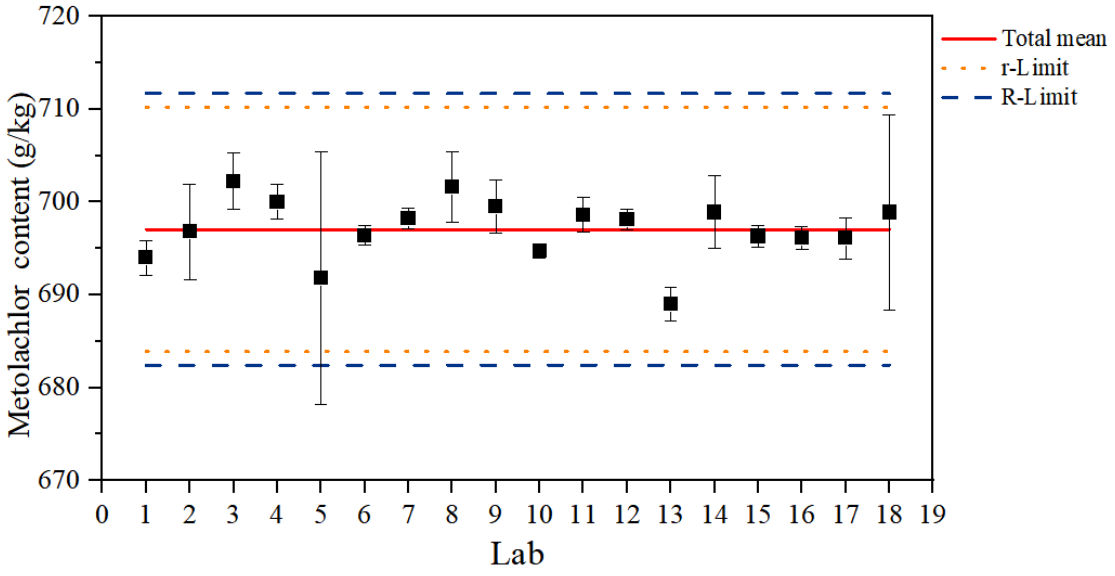


Figure 5. Graphical presentation of EC3 data

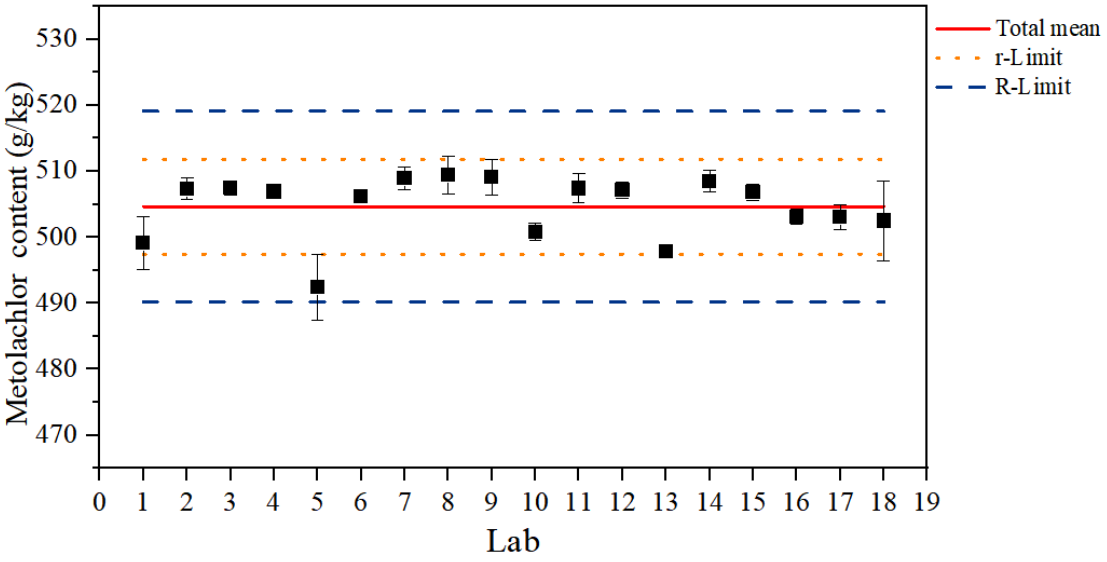


Figure 6. Graphical presentation of EW1 data

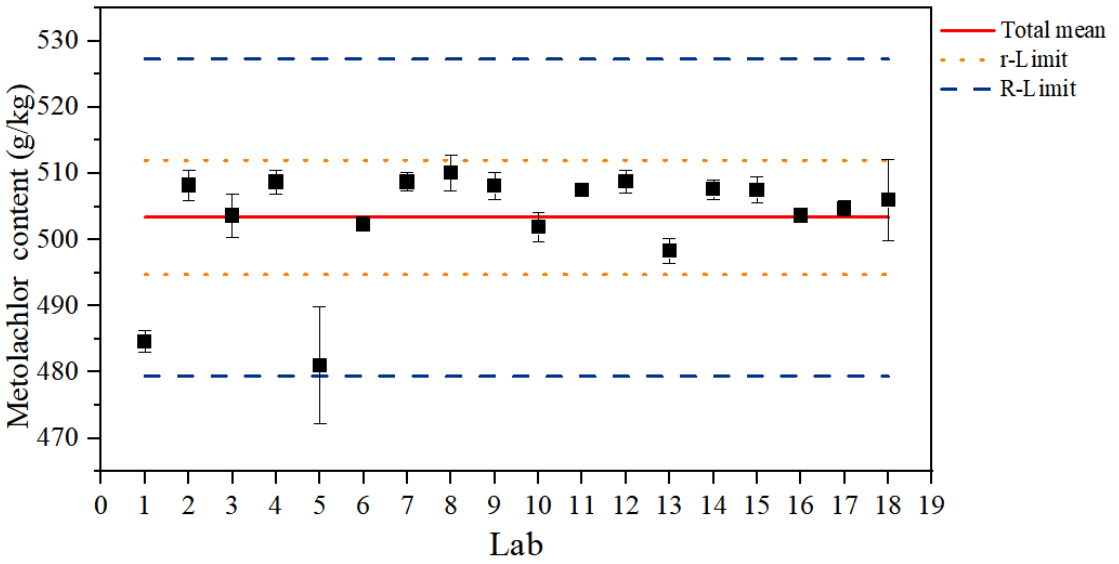


Figure 7. Graphical presentation of EW2 data

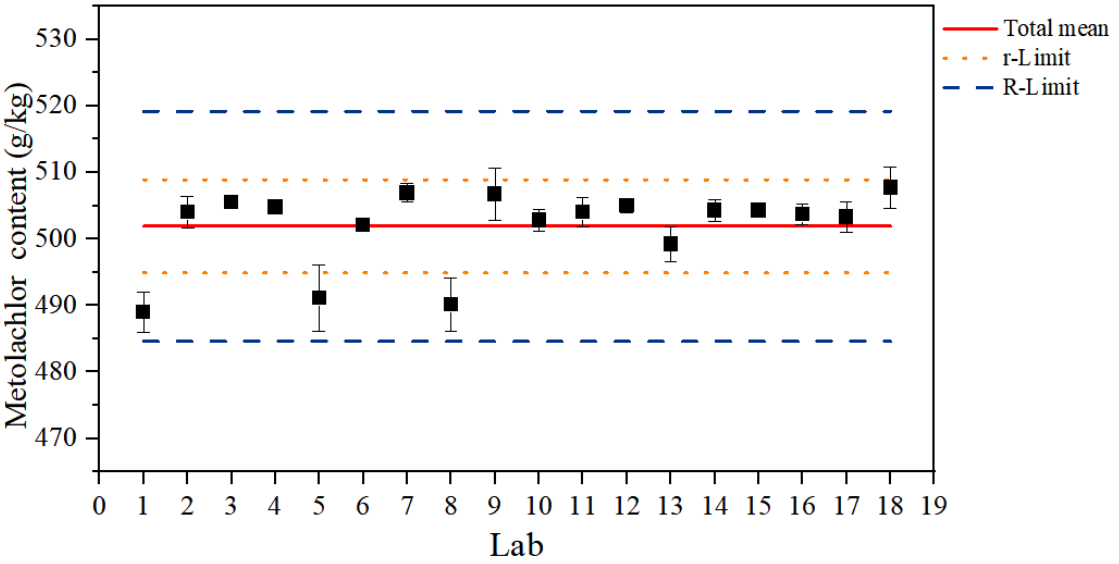


Figure 8. Graphical presentation of EW3 data

7. Conclusions

18 different laboratories participated in this collaborative study. The results of the labs are given in Table 1-2, the statistical summary is given in Table 3-4. The results are illustrated in figures 1–8.

Without elimination of any outliers and stragglers, the between-lab experimental Reproducibility Relative Standard Deviation (% RSD_R) is below the calculated acceptable value based on the Horwitz curve calculation (% RSD_R (Hor) for all samples. Considering the validation criteria are fulfilled, no elimination of outliers and stragglers are processed. The HorRat values were smaller than 1.0 by employing this method. The minimum number of considered results was 18.

Taking into account the relatively high number of participating laboratories a broad basis was given. Therefore, CHIPAC considers this method to be suitable and recommend accepting it as a provisional CIPAC method for the determination of Metolachlor in both technical materials and its associated formulated products （EC.EW）.