Determination of Quizalofop-p-ethyl Active in TC and EC

Small Scale Collaborative Study for the Determination of Quizalofop-p-ethyl Active in TC and EC by GC and HPLC

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1. Participants

Name of responsible person	Lab Name	City, Country
Huang Liang	Anhui Fengle Agrochemical Co., Ltd. Product Testing Center	Anhui, China
Zhou Tao	Anhui Huachen Testing Technology Research Institute Co., Ltd.	Anhui, China
Deng Xilan	Jiangsu Repont Chemical Co.,Ltd. Product Testing Center	Jiangsu, China
Duan liangju	Anhui Jiuyi Agriculture Co.,Ltd. Product Testing Center	Anhui, China

Laboratories were identified by a confidential number prior to the trial commencing

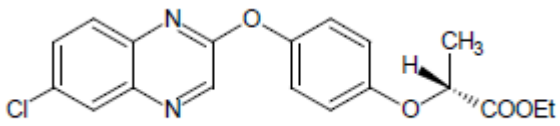
2. Active Ingredient, General Information

IUPAC name: ethyl (R)-2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propionate

ISO common name: Quizalofop-p-ethyl

CAS-Nr.: 100646-51-3

Structure:



Molecular mass: 372.8

Empirical formula: $C_{19}H_{17}ClN_2O_4$

3. Samples

In Apr 2019 the following samples were sent to the participants:
Describe sample:

TC: white to yellow powder

EC: Homogeneous liquid with aromatic hydrocarbon odor

In 19/20.04.2019 results were obtained.

4. Method

4.1 Scope

Determination of the content of the active level in TC and EC.

Quizalofop-ethyl is determined by gas chromatography using FID detector and di-n-octyl phthalate as internal standard. Quizalofop-p-ethyl (R-enantiomer) is separated from the s-enantiomer and is determined by normal phase HPLC on chiral column using UV detector at 237 nm and external standardization.

4.2 Principle

Step 1:
Use the gas chromatography method below. The retention time of Quizalofop-ethyl peak in the sample solution should not deviate by more than 1.5% from that for the calibration solution.

Step 2:
Use the HPLC method below. The retention time of Quizalofop-p-ethyl peak in the sample solution should not deviate by more than 1.5% from that for the calibration solution.

4.3 Procedure for the collaborative trial

The sample were analyzed on two different days with duplicate injections weighting per. Sample Test and reference solutions were prepared fresh on each day. The sample content was calculated using the mean value of the duplicate injections.

5. Analytical conditions

Step 1:

Lab No	Column	Temperature (Column, Detector, Injector, ℃)	Gas flow rates(Carrier gas (high purity Nitrogen), Hydrogen, Air, ml/min)	Injection vol. (µl)
1	Agilent HP-5, (5%- phenyl) - methyl polysiloxane; 15 m *0.53 mm* 1.5 µm Part Number: 19095J-321	250, 250, 250	15(7 for EC), 30, 300	1.0
2	Agilent HP-5, (5%- phenyl) - methyl polysiloxane; 15 m*0.53 mm*1.5 µm Part number: 19095J-321	250, 250, 250	15, 30, 300	1.0
3	Agilent HP-5, (5%- phenyl) - methyl polysiloxane; 30 m*0.32 mm*0.25 µm Part Number: 19091J-413	270, 270, 300	1.6, 30, 300	0.4
4	RTX-5, (5%- phenyl) - methyl polysiloxane; 30 meter, 0.32 mmID, 0.25 µmDF	240, 250, 250	5, 30, 400	0.4

Step 2:

Lab No	Column	Mobil phase	Flow rate ml/min	Column temp. (℃)	Injection vol. (µl)
1	Column stainless steel: 250 mm * 4.6 mm (id), CHIRALPAK AD-H, 5 µm	n-hexane + Isopropanol = 90 + 10 (v/v)	0.6	25	5.0
2	CHIRALPAK AD-H (DAICEL CHEMICAL IND LTD, 4.6 mm*250 mm) Part No：19325	n-hexane + Isopropanol = 90 + 10 (v/v)	0.6	35	5.0
3	CHIRALCEL OJ-H, DAICEL CORPORATION 250*4.6 mm	n-hexane + ethyl alcohol= 90 + 10 (v/v)	1.4	30	5.0
4	Column stainless steel: 250 mm * 4.6 mm (id), CHIRALPAK AD-H, 5 µm	n-hexane + Isopropanol = 90 + 10 (v/v)	0.6	30	5.0

6. Remarks of the Participants

Several participants made comments about the performance of the method and noted deviations from the method:

Laboratory 1	Step 1: Column: Agilent HP-5 15 m*0.53 mm*1.5 µm Part number: 19095J-321 Remarks: Gas flow rates(Carrier gas): 7 ml/min for EC Step 2: Column stainless steel: 250 mm X 4.6 mm (id), Lot No.ADH0CE-QD122, CHIRALPAK AD-H, 5 µm Remarks: None
Laboratory 2	Step 1: Column: Agilent HP-5, 15 m*0.53 mm*1.5 µm Part number: 19095J-321 Remarks: None Step 2: CHIRALPAK AD-H(DAICEL CHEMICAL IND, LTD, 4.6 mm*250 mm) Part No: 19325 Remarks: Injection vol. 2.0 µl
Laboratory 3	Step 1: Column: Agilent HP-5, 30 m*0.32 mm*0.25 µm; Part Number: 19091J-413 Remarks: Temperature(Column, Detector, Injector, °C): 270, 270, 300; Gas flow rates(Carrier gas (high purity Nitrogen), ml/min): 1.6; Injection vol. 0.4 µl Step 2: Column: CHIRALCEL OJ-HDAICEL; CORPORATION 250*4.6 mm Remarks: Flow rate 1.4 ml/min
Laboratory 4	Step 1: Column: RTX-5 30 meter, 0.32 mmID, 0.25 µmDF Remarks: Temperature(Column, °C): 240; Gas flow rates(Carrier gas (high purity Nitrogen), Air, ml/min):5,400; Injection vol. 0.4 µl Step 2: Column stainless steel: 250 mm X 4.6 mm (id), CHIRALPAK AD-H, 5 µm Remarks: None

7. Evaluation and Discussion

The full results of four labs were included within the statistical assessment. The statistical evaluation of the data was accomplished following the “Guidelines for CIPAC Collaborative Study Procedures for Assessment of Performance of Analytical Methods”, according to DIN ISO 5725.

The assay results obtained by the collaborators and the statistical evaluation are reported in Table 1 and Tables 2-1 to 2-5. There is no stragglers or outliers in technical material and EC formulation.

8. Conclusions

For all samples, the values of RSD_R (reproducibility relative standard deviation) were less than Horwitz’s value. As a reference, all HorRat values were not greater than 1.0. The proposed method is considered to be appropriate for the determination of Quizalofop-p-ethyl in technical material and EC formulation.

CHIPAC proposes to proceed with a large scale collaborative study.

9. Appendix A

Tables and Figures for Quizalofop-p-ethyl.

Table 1: Summary of the statistical evaluation

	TC-1	TC-2	EC-1	EC-2	EC-3
Xm	965.9	961.3	102.3	101.4	107.1
L	4	4	4	4	4
S_r	2.506	2.395	1.160	1.098	1.277
S_R	3.139	3.137	1.200	1.569	2.064
r	7.017	6.705	3.249	3.075	3.575
R	8.790	8.782	3.360	4.394	5.780
RSD_r	0.259	0.249	1.135	1.083	1.193
RSD_R	0.325	0.326	1.174	1.547	1.928
RSD_R (Hor)	2.010	2.012	2.819	2.822	2.800
HorRat Value	0.16	0.16	0.42	0.55	0.69

Xm = average

L = number of laboratories

S_r = repeatability standard deviation

S_R = reproducibility standard deviation

RSD_r = repeatability relative standard deviation

RSD_R = reproducibility relative standard deviation

r = repeatability

R = reproducibility

RSD_R (Hor) = Horwitz value calculated from: 2^(1 - 0.5log c) where c = the concentration of the analyte as a decimal fraction

Table 2-1 Quizalofop-p-ethyl Technical-1

Lab	Analytical data (n=4)			Yi	Yi^2	Si	Si^2
1	Day1	968.3	967.1				
	Day2	964.1	968.5	967.0	935089.00	2.030	4.120
2	Day1	966.4	970.0				
	Day2	964.8	972.6	968.5	937895.40	3.519	12.383
3	Day1	967.6	963.6				
	Day2	960.9	962.2	963.6	928476.78	2.901	8.416
4	Day1	963.8	964.4				
	Day2	964.4	964.9	964.4	930019.14	0.450	0.203
S1	sum Yi			3963.4			
S2	sum Yi^2				3731480.32		
S3	sum Si^2						25.122

p=4 n=4

1) Grubbs's test (p=4, n=4)

Yi min=	963.6	Yi max=	968.5	Y=	965.9
Y-Yi min=	2.2	Yi max-Y=	2.7	S=	2.268
lower=	0.992	< 1.48 (p=4, 5%)			
upper=	1.168	< 1.48 (p=4, 5%)			

2) Calculation of r and R

Mean: Y=S1/p=		965.9		
S_r^2=	S3/p=	6.280	S_r=	2.506
S_L^2=	[(pS2-S12)/p(p-1)]- S_r^2/n=	3.574	S_L=	1.891
S_R^2=	$S_r^2+S_L^2$=	9.855	S_R=	3.139

r=	$2.8*S_r$=	7.017
R=	$2.8*S_R$=	8.790
RSD_r=	(S_r/mean)*100=	0.259
RSD_R=	(S_R/mean)*100=	0.325

Horwitz's value= 2^[1-0.5*log(Y/1000)] = 2.010
RSD_r and RSD_R < 2.010 (Horwitz's value)
HorRat value= RSD_R/Horwitz's value= 0.16

Table 2-2 Quizalofop-p-ethyl Technical-2

Lab	Analytical data (n=4)			Yi	Yi^2	Si	Si^2
1	Day1	963.3	959.1				
	Day2	961.9	963.7	962.0	925444.00	2.082	4.333
2	Day1	960.0	957.6				
	Day2	955.2	958.3	957.8	917332.95	1.991	3.962
3	Day1	962.7	968.3				
	Day2	959.7	961.2	963.0	927320.85	3.755	14.102
4	Day1	962.1	963.3				
	Day2	962.0	961.6	962.3	925925.06	0.733	0.537
S1	sum Yi			3845.0			
S2	sum Yi^2				3696022.86		
S3	sum Si^2						22.935

p=4 n=4

1) Grubbs's test (p=4, n=4)

Yi min=	957.8	Yi max=	963.0	Y=	961.3
Y-Yi min=	3.5	Yi max-Y=	1.8	S=	2.353
lower=	1.466	< 1.48 (p=4, 5%)			
upper=	0.744	< 1.48 (p=4, 5%)			

2) Calculation of r and R

Mean: Y=S1/p=		961.3		
S_r^2=	S3/p=	5.734	S_r=	2.395
S_L^2=	$[(pS2-S12)/p(p-1)]- S_r^2/n$=	4.104	S_L=	2.026
S_R^2=	$S_r^2+S_L^2$=	9.838	S_R=	3.137

r=	$2.8*S_r$=	6.705
R=	$2.8*S_R$=	8.782
RSD_r=	$(S_r/mean)*100$=	0.249
RSD_R=	$(S_R/mean)*100$=	0.326

Horwitz's value= 2^[1-0.5*log(Y/1000)]= 2.012
RSD_r and RSD_R < 2.012(Horwitz's value)
HorRat value= RSD_R/Horwitz's value= 0.16

Table 2-3 Quizalofop-p-ethyl EC-1

Lab	Analytical data (n=4)			Yi	Yi^2	Si	Si^2
1	Day1	101.6	105.7	103.2	10650.24	1.757	3.087
	Day2	102.9	102.6				
2	Day1	103.3	102.0	101.7	10342.89	1.299	1.687
	Day2	100.2	101.3				
3	Day1	101.6	101.7	102.2	10434.62	0.592	0.350
	Day2	102.5	102.8				
4	Day1	101.9	102.5	102.0	10398.90	0.512	0.263
	Day2	102.2	101.3				
S1	sum Yi			409.0			
S2	sum Yi^2				41826.65		
S3	sum Si^2						5.386

p=4 n=4

1) Grubbs's test (p=4, n=4)

Yi min=	101.7	Yi max=	103.2	Y=	102.3
Y-Yi min=	0.6	Yi max-Y=	0.9	S=	0.656
lower=	0.848	< 1.48 (p=4, 5%)			
upper=	1.439	< 1.48 (p=4, 5%)			

2) Calculation of r and R

Mean: Y=S1/p=		102.3		
S_r^2=	S3/p=	1.346	S_r=	1.160
S_L^2=	[(pS2-S12)/p(p-1)]- S_r^2/n=	0.094	S_L=	0.306
S_R^2=	$S_r^2+S_L^2$=	1.440	S_R=	1.200

r=	2.8*S_r=	3.249
R=	2.8*S_R=	3.360
RSD_r=	(S_r/mean)*100=	1.135
RSD_R=	(S_R/mean)*100=	1.174

Horwitz's value= 2^[1-0.5*log(Y/1000)]= 2.819
RSD_r and RSD_R < 2.819（Horwitz's value)
HorRat value= RSD_R/Horwitz's value= 0.42

Table 2-4 Quizalofop-p-ethyl EC-2

Lab	Analytical data (n=4)			Yi	Yi^2	Si	Si^2
1	Day1	101.0	100.2	101.4	10271.82	0.929	0.863
	Day2	102.2	102.0				
2	Day1	105.1	104.0	102.9	10593.56	1.957	3.829
	Day2	101.7	100.9				
3	Day1	101.6	101.5	101.6	10312.40	0.208	0.043
	Day2	101.8	101.3				
4	Day1	99.8	100.2	99.9	9975.02	0.299	0.089
	Day2	99.5	100.0				
S1	sum Yi			405.7			
S2	sum Yi^2				41152.80		
S3	sum Si^2						4.825

p=4 n=4

1) Grubbs's test (p=4, n=4)

Yi min=	99.9	Yi max=	102.9	Y=	101.4
Y-Yi min=	1.5	Yi max-Y=	1.5	S=	1.248
lower=	1.222	< 1.48 (p=4, 5%)			
upper=	1.182	< 1.48 (p=4, 5%)			

2) Calculation of r and R

Mean: Y=S1/p=		101.4		
S_r^2=	S3/p=	1.206	S_r=	1.098
S_L^2=	[(pS2-S12)/p(p-1)]- S_r^2/n=	1.256	S_L=	1.121
S_R^2=	S_r^2+S_L^2=	2.463	S_R=	1.569

r=	2.8*S_r=	3.075
R=	2.8*S_R=	4.394
RSD_r=	(S_r/mean)*100=	1.083
RSD_R=	(S_R/mean)*100=	1.547

Horwitz's value= 2^[1-0.5*log(Y/1000)]= 2.822
RSD_r and RSD_R < 2.822（Horwitz's value)
HorRat value= RSD_R/Horwitz's value= 0.55

Table 2-5 Quizalofop-p-ethyl EC-3

Lab	Analytical data (n=4)			Yi	Yi^2	Si	Si^2
1	Day1	106.9	108.4	106.8	11406.24	1.393	1.940
	Day2	106.9	105.0				
2	Day1	111.7	109.1	109.1	11908.27	2.043	4.176
	Day2	106.7	109.0				
3	Day1	106.8	107.6	107.4	11534.76	0.432	0.187
	Day2	107.4	107.8				
4	Day1	104.7	105.5	104.9	11004.01	0.469	0.220
	Day2	105.0	104.4				
S1	sum Yi			428.2			
S2	sum Yi^2				45853.28		
S3	sum Si^2						6.523

p=4 n=4

1) Grubbs's test (p=4, n=4)

Yi min=	104.9	Yi max=	109.1	Y=	107.1
Y-Yi min=	2.2	Yi max-Y=	2.0	S=	1.743
lower=	1.237	< 1.48 (p=4, 5%)			
upper=	1.173	< 1.48 (p=4, 5%)			

2) Calculation of r and R

Mean: Y=S1/p=		107.1		
S_r^2=	S3/p=	1.631	S_r=	1.277
S_L^2=	[(pS2-S12)/p(p-1)]- S_r^2/n=	2.630	S_L=	1.622
S_R^2=	$S_r^2+S_L^2$=	4.261	S_R=	2.064

r=	2.8*S_r=	3.575
R=	2.8*S_R=	5.780
RSD_r=	(S_r/mean)*100=	1.193
RSD_R=	(S_R/mean)*100=	1.928

Horwitz's value= 2^[1-0.5*log(Y/1000)]= 2.800

RSD_r and RSD_R < 2.800（Horwitz's value)

HorRat value= RSD_R/Horwitz's value= 0.69

Fig. 1: Results of the Quizalofop-p-ethyl TC-1(see table 2 for the evaluation)

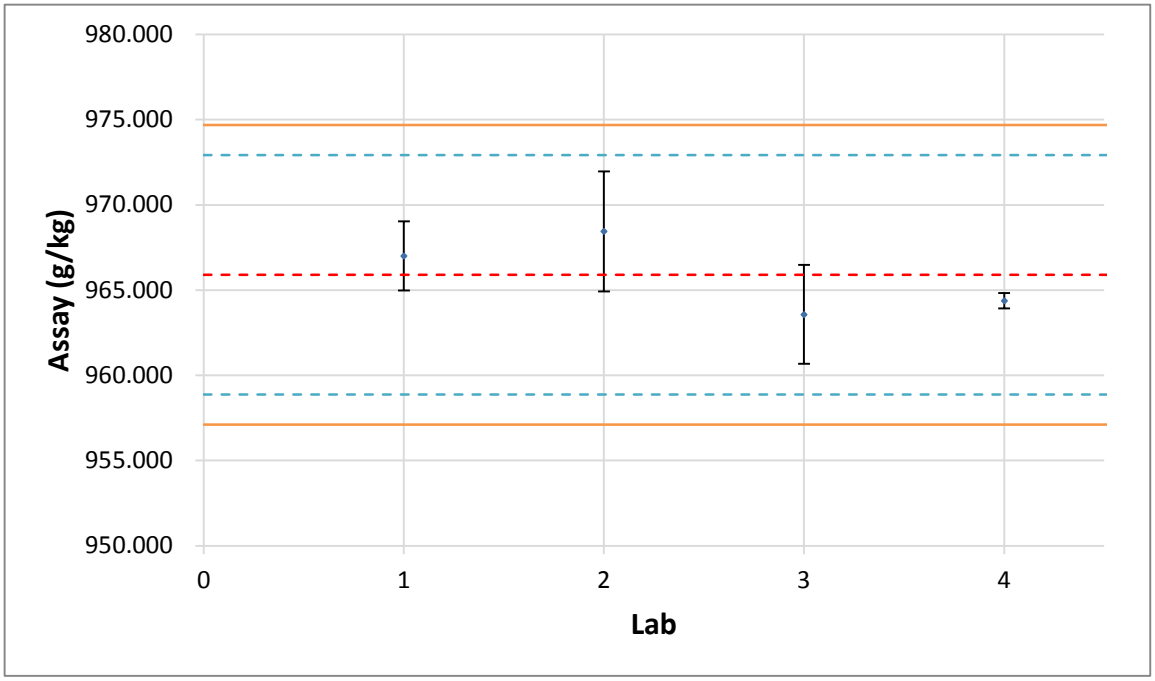


Fig. 2: Results of the Quizalofop-p-ethyl TC-2(see table 2 for the evaluation)

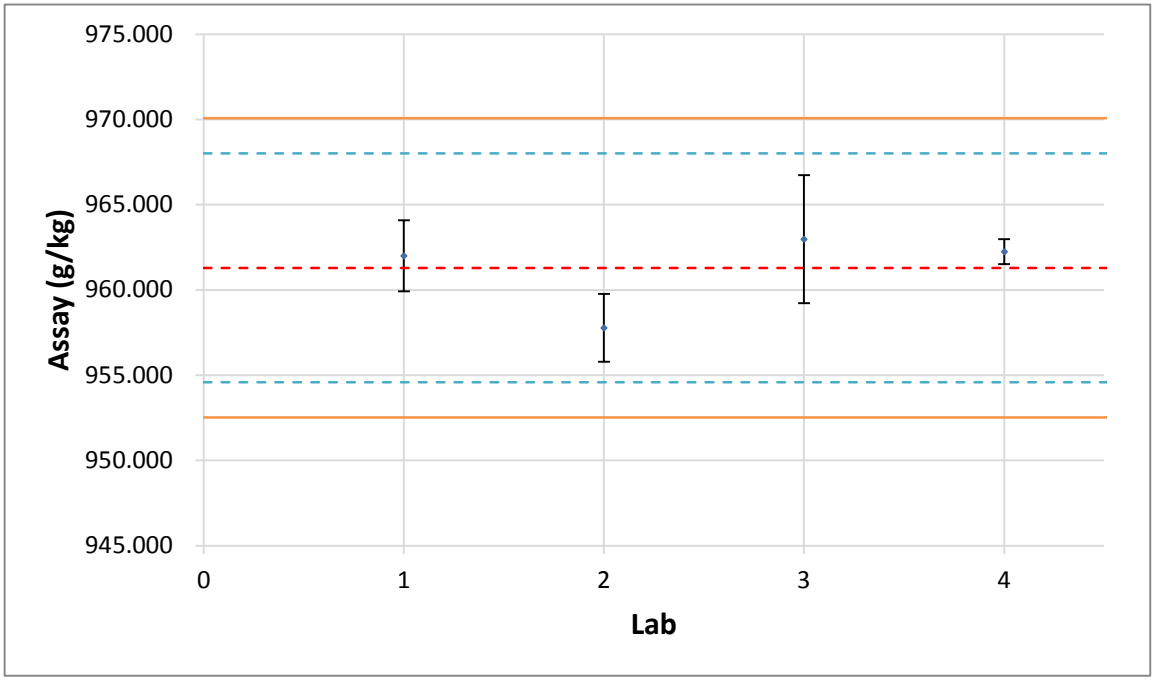


Fig. 3: Results of the Quizalofop-p-ethyl EC-1(see table 2 for the evaluation)

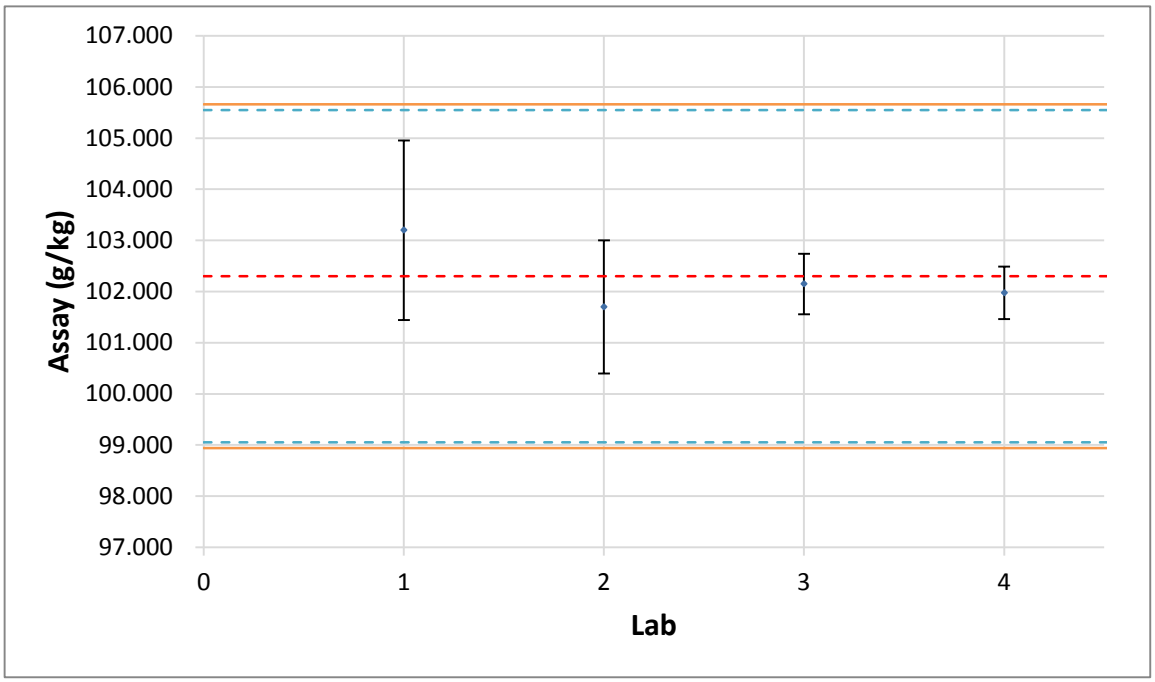


Fig. 4: Results of the sample EC-2(see table 2 for the evaluation)

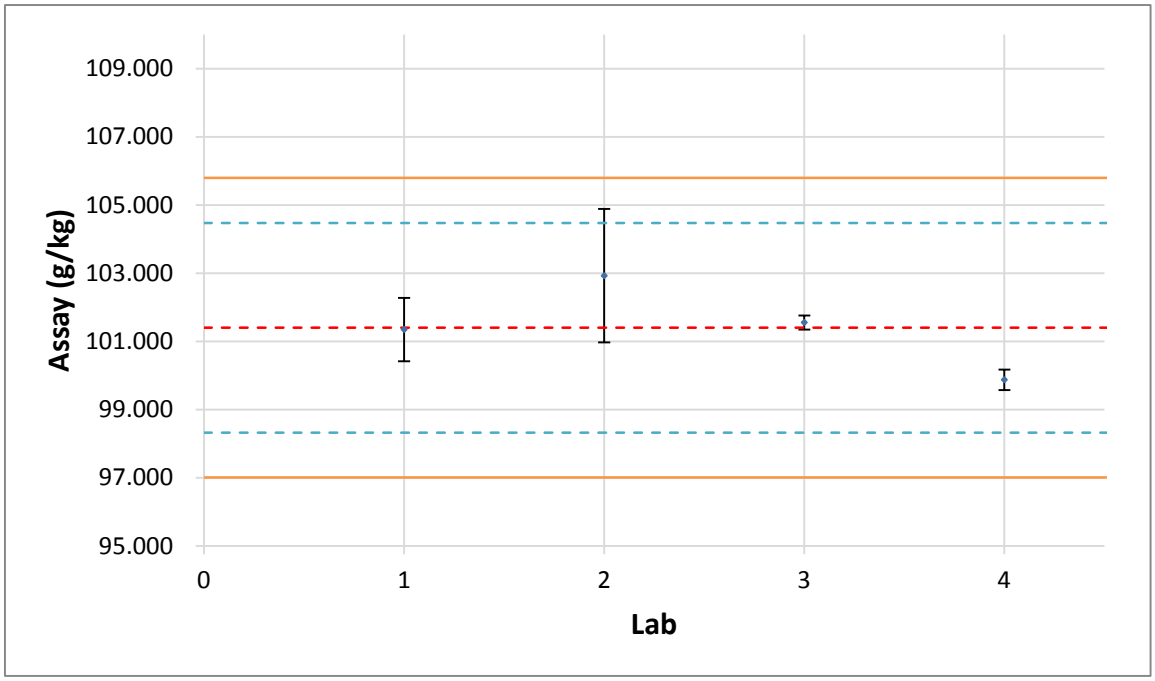


Fig. 5: Results of the sample EC-3(see table 2 for the evaluation)