

METRIBUZIN

Collaborative Study

Full Scale Collaborative Study
for the
Determination of Metribuzin TC and formulations, by
Gas Chromatography

Report to CIPAC
by
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1. Participants

In September 2019, Information Sheet No. 321 was sent out by the CIPAC Secretary inviting members to participate in a collaborative study on the determination of Metribuzin, by capillary gas chromatography.

Originally the trial has been limited to a maximum of 15 laboratories by the organizer and due to the availability of samples. Due to the great interest in participating the trial was extended to a maximum of 18 laboratories.

By mid of April 2020, 17 of the 18 selected laboratories provided their results.

- One participant could not reply in time due to restrictions caused by the COVID-19 crisis.

The results of the 17 participants are presented in the following sections.

Participating laboratories are listed in alphabetical order in the table below whereas lab numbers in the result tables were assigned, chronologically, based upon receipt of results.

Greco, Cornel	ALCHIMEX S.A. 63-Alexandru Constantinescu, sector 1 011472 Bucharest Romania
Schaller, Ulrich	Agroscope Pflanzenschutzchemie Müller-Thurgau-Strasse 29 8820 Wädenswil Switzerland
Schulz, Friedhelm	Bayer AG, Crop Science Division Research & Development, Small Molocules Research, Product Chemistry Analytics Alfred-Nobel-Str. 50, 40789 Monheim am Rhein Germany
Vinke, Claudia	Bundesamt für Verbraucherschutz und Lebensmittelsicherheit Referat Pflanzenschutz Messeweg 11/12, 38104 Braunschweig Germany
Karassali, Helen	Benaki Phytopathological Institute 8 Stefanou Delta street, 14561 Kifissia, Athens Greece

Haustein, Michael	Currenta GmbH & Co. OHG Division Analytics, Production Analytics 41538 Dormagen Germany
Osterballe Pedersen, Christina	Danish Technological Institute Teknologisk Institut Kemisk og Mikrobiologisk Laboratorium Kongsvang Allé 29 8000 Aarhus C Denmark
Santilio, Angela	Istituto Superiore di Sanità (National Institute of Health) Department of Environment and Health (Dipartimento Ambiente e Salute) ECASS Section (Reparto ECASS) Viale Regina Elena, 299 00161 Rome Italy
Lee, Jacky	Jiangsu Seven Continent 7F, Guotai Times Plaza A, Renmin Road, Zhangjiagang, Jiangsu Province, China
Belart, Selma	Laboratorio de Plaguicidas y Formulados SENASA Av. Huergo 1001 - 1107 CABA Argentina
McManus, Kenneth	Maryland Department of Agriculture 50 Harry S Truman Parkway Annapolis, MD 21401 USA
Ciotea, Florentina	National Phytosanitary Authority Voluntari Bvd. No. 11, Voluntari Town, Ilfov County, Romania
Li, Hongxia	Nutrichem Laboratory Co., Ltd. No. 27, Life Science Park Road, Changping Dist., Beijing 102206 China

Joseph, Rachel	ROTAM RESEARCH LABORATORY No. 233, Songjiagang Road, Zhoushi Town, Kunshan, Jiangsu China
Garvey, Jim	Pesticide Control Laboratory, Department of Agriculture, Food and the Marine Backweston Laboratory Complex, Backweston, Celbridge, Co. Kildare, Ireland
Mink, Christian	Syngenta Crop Protection AG Breitenloh 5, 4333 Münchwilen Switzerland
Novakova, Olga	UKZUZ (CENTRAL INSTITUTE FOR SUPERVISING AND TESTING IN AGRICULTURE) National Reference Laboratory Department of Testing Plant Protection Products Zemědělská 1a, 613 00 Brno Czech Republic

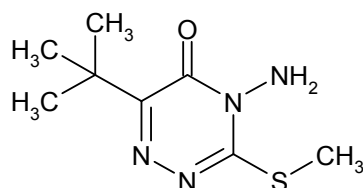
2. Active Ingredient: General Information

Chemical name: 4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one

ISO common name: metribuzin

CAS-No.: 21087-64-9

Structure:



Molecular mass: 214.3 g/mol

Empirical formula: C₈ H₁₄ N₄ O S

Activity: Herbicide

3. Samples

Nine test samples, Metribuzin analytical standard and internal standard Dipentylphthalate were sent to the participants (in brackets: sample description used in the following tables)

1. Metribuzin tech. sample – 1 (Metribuzin TC_1)
2. Metribuzin tech. sample – 2 (Metribuzin TC_2)
3. Metribuzin WG 70 – 1 (Metribuzin WG 70)
4. Metribuzin WG 70 – 2 (Metribuzin 70 % WG)
5. Metribuzin WP 70 – 1 (Metribuzin WP 70)
6. Metribuzin WP 70 – 2 (Metribuzin 70 % WP)
7. Metribuzin SC 600; 522 g/kg Metribuzin (Metribuzin SC 600)
8. Metribuzin SC 480 – 1; 414 g/kg Metribuzin (Metribuzin SC 480)
9. Metribuzin SC 480 – 2 (Metribuzin 42 % SC)

Metribuzin, reference standard (purity 93.8 %w/w)

Internal Standard, Dipentylphthalate, 2 x 1 mL

4. Method

4.1 Scope

The determination of Metribuzin active ingredient content in technical grade material (TC) and SC, WG, WP formulations.

4.2 Principle

Metribuzin content is by capillary gas chromatography with split injection, using dipentylphthalate as internal standard.

4.3 Procedure

Each sample was analyzed using four independent determinations. The samples were analyzed on two different days, each day involving duplicate injections of duplicate weights. Both test and reference solutions were freshly prepared on each day. The four injections of each test solution were bracketed by double injections of the calibration solution. The average response factor, used to calculate the amount of Metribuzin in the test solution, was calculated using the injection before and after the test injections.

5. Remarks of the Participants

Several participants provided comments about the method performance and also made a note of any deviations from the method:

Laboratory 1	Column:	Restek RTX-5 (30 m, 0.25 µm film, 0.25 mm ID)
	Remarks:	WG samples mortrated with an agate mortar; equilibration day 1 done, but forgotten to create printed data, overwritten with day 2, equilibration day 2 made with calibration solution 1 of day 1..
Laboratory 2	Column:	J&W DB-5 (30 m, 0.25 µm film, 0.32 mm ID)
	Remarks:	Peaks with fronting: Metribuzin assym 0.65, IS 0.79; WG, WP, SC: 5 min ultra sonic bath and 3 min centrifugation at 6000 rpm, SC: additional 5 min ultra sonic bath after adding 0.5 mL water, if split 1:100, then peaks with less fronting: Metribuzin assym 0.74, IS 0.91
Laboratory 3	Column:	DB-5 (30 m, 0.25 µm film, 0.32 mm ID)
	Remarks:	Day 2: weighing of SC formulations was performed taking the density of 1.16 g/mL into account; sample order of day 2 changed
Laboratory 4	Column:	HP-5 (30 m, 0.25 µm film, 0.32 mm ID)
	Note:	Hydrogen used as carrier gas
	Remarks:	Make up gas was nitrogen in which was approved by the sponsor I would adjust the GC parameters for better chromatography by having the retention times of analytes of interest further away from that of solvent and other interferences
Laboratory 5	Column:	DB-5 (30 m, 0.25 µm film, 0.32 mm ID)
	Remarks:	None
Laboratory 6	Column:	MN Optima 5 (30 m, 0.25 µm film, 0.32 mm ID)
	Remarks:	Make up gas: Nitrogen 30 mL/min WG and WP samples were filtered with chromafil xtra PTFE-45/25 0.25 µm filter

Laboratory 7	Column:	DB-5 MS (30 m, 0.25 µm film, 0.25 mm ID)
	Remarks:	We observe that the profile of the chromatographic peaks varies in the course a sequence and suspect that this may be caused by the injection – possibly the 1 µL syringe is not functioning optimally on our system. For most of the injections the IS adequately compensates for this problem and we have therefore opted to stay loyal to the method description rather than trying to optimize the method to our conditions.
Laboratory 8	Column:	Thermo TG-5 MS (30 m, 0.25 µm film, 0.32 mm ID)
	Remarks:	None
Laboratory 9	Column:	HP-5 MS (30 m, 0.25 µm film, 0.25 mm ID)
	Remarks:	None
Laboratory 10	Column:	HP-5 (30 m, 0.25 µm film, 0.32 mm ID)
	Remarks:	Nitrogen was used instead of helium
Laboratory 11	Column:	DB-5 (30 m, 0.25 µm film, 0.32 mm ID)
	Note:	Nitrogen used as carrier gas
	Remarks:	None
Laboratory 12	Column:	DB-1 (30 m, 0.25 µm film, 0.32 mm ID)
	Remarks:	None
Laboratory 13	Column:	DB-5 (30 m, 0.25 µm film, 0.32 mm ID)
	Note:	Nitrogen used as carrier gas
	Remarks:	None
Laboratory 14	Column:	TR-5 MS (30 m, 0.32 mm ID)
	Remarks:	We used nitrogen instead of helium.
Laboratory 15	Column:	Zebtron ZB-5 (30 m, 0.25 µm film, 0.32 mm ID)

Remarks: All samples and standard solutions were ultrasonicated for 15 min. All WG and WP samples were filtered due to no completed solution (0.45 μm). For the day 2 the SC 42 % and SC 600 samples were filtered due to streaking (0.45 μm)

In the method description for SC it is given that the sample should first be suspended in 0.5 mL purified water and then 10 mL internal standard solution has to be added. Therefore the total volume of solvent is higher than for the other samples. But the factor in the calculation sheet for the SC samples is 10 too.

Laboratory 16	Column:	DB-1 (30 m, 1.5 µm film, 0.53 mm ID)
	Remarks:	None
Laboratory 17	Column:	DB-5 (30 m, 0.25 µm film, 0.25 mm ID)
	Note:	Nitrogen used as carrier gas
	Remarks:	with DB-5 of 0.25 µm film thickness, 0.32 mm film id (as recommended in the method) AI peak showed split. Changed to HP-5 of 0.25 µm film thickness, 0.32 mm film id, and also observed split in AI peak With the above 2 columns using DCM as solvent gives sharp peak As peak split was observed with 0.32 mm i.d., we changed to column of 0.25 mm i.d. we tried with 0.2 µL and 1 µL injection volumes and found that variations between injections are less with 1 µL. For FID methods usually 1 µL is used. We tried testing SC as in method 10.5 mL total volume Vs calibration solution 10 ml and compared the results by making up both the calibration and SC to constant volume of 25 ml – No significant differences in the results were observed.

6. Evaluation and Discussion

6.1 Data Review

The data obtained from each laboratory was visually reviewed to determine if there were any significant chromatography differences, from what was expected, which might affect the analytical results.

In summary it can be stated that the method deviations, noted by the participants, were deemed not to affect the analytical results significantly and therefore all data sets were included within the statistical assessment. However, it is obvious that change of the carrier gas from Helium to Hydrogen or Nitrogen, respectively, lowers the total reproducibility leading to a short failure of the HorRat criterion in 2 of 9 samples.

Therefore, the report below contains both statistical evaluations, once with the full set of participating laboratories (17) and twice with the 11 participants using Helium as a carrier gas.

6.2 Determination of Metribuzin

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 testing for outliers/stragglers of the laboratory mean values were performed according to Grubbs test on a 1%/5% significance level, respectively.

In the tables 1-9 and figures 1-9, respectively, the full set of all laboratories (17 participants) are reported. No outliers could be detected, but laboratory 4 three times was identified as lower straggler according to Grubbs test. The Horwitz Ratio (HorRat) was found within the desired range (≥ 0.3 but ≤ 1.0) apart from two samples where a HorRat above 1.0 up to 1.2 was determined. It should be noticed that this effect is not specific for a certain formulation type.

In a second evaluation (tables 10-18 and figures 10-18) the data of the 11 laboratories using Helium as a carrier gas, as described by the method, are reported. The other 6 laboratories including laboratory 4 which used Hydrogen, were not taken into account. By this, a significant improvement of the HorRat values of most of the samples was observable (table 19).

Determination of Metribuzin – full set of 17 participants

All results are given in g/kg

Table 1 Results

	Metribuzin TC_1		Metribuzin TC_2		Metribuzin WG 70		Metribuzin 70 % WG	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Laboratory 1	963.9	960.6	995.5	988.4	676.0	675.6	710.6	709.0
Laboratory 2	964.6	964.5	995.0	995.1	687.6	689.1	713.4	711.7
Laboratory 3	969.6	973.2	1002.1	997.9	690.9	689.3	712.2	710.3
Laboratory 4	935.4	926.8	965.0	987.6	632.6	648.2	697.8	701.6
Laboratory 5	964.7	963.6	993.9	992.5	686.5	687.5	708.2	710.6
Laboratory 6	960.8	962.4	989.6	990.4	684.5	686.3	710.0	711.6
Laboratory 7	946.2	939.2	977.5	941.5	668.0	636.2	695.9	711.4
Laboratory 8	957.7	959.6	990.7	990.6	691.4	686.4	710.8	704.6
Laboratory 9	970.5	975.4	996.5	992.9	692.0	697.8	720.5	721.6
Laboratory 10	962.7	959.6	991.3	985.3	688.1	683.4	708.8	706.3
Laboratory 11	977.6	952.5	982.5	987.3	695.7	685.6	707.8	706.2
Laboratory 12	967.1	984.6	966.1	981.1	680.8	678.3	698.6	700.3
Laboratory 13	945.1	946.2	973.5	971.1	678.8	677.1	714.7	714.7
Laboratory 14	968.9	965.5	1003.4	1008.8	706.8	689.3	729.9	716.7
Laboratory 15	966.1	957.0	991.9	982.0	692.6	686.8	713.9	719.9
Laboratory 16	972.4	972.4	971.1	971.5	699.9	702.8	702.5	699.9
Laboratory 17	972.5	964.4	970.9	971.8	696.9	711.8	703.3	702.5

Table 2 Results

	Metribuzin WP 70		Metribuzin 70 % WP		Metribuzin SC 600 (522 g/kg Metribuzin)	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Laboratory 1	711.0	706.8	709.8	707.7	533.6	534.8
Laboratory 2	712.9	712.4	714.6	713.5	531.4	529.2
Laboratory 3	718.5	710.0	711.7	711.7	537.0	534.0
Laboratory 4	674.9	690.7	691.6	699.1	505.6	523.2
Laboratory 5	708.8	711.0	708.4	708.7	527.1	528.1
Laboratory 6	710.7	712.6	707.8	710.2	528.6	531.8
Laboratory 7	695.0	709.2	693.8	710.8	523.8	534.4
Laboratory 8	713.3	708.2	712.1	714.1	530.3	526.1
Laboratory 9	721.9	726.2	716.0	725.2	536.0	551.1
Laboratory 10	709.7	708.9	710.3	710.1	532.3	532.4
Laboratory 11	704.0	711.0	705.1	697.7	530.7	532.8
Laboratory 12	699.9	700.5	701.7	690.9	525.2	524.6
Laboratory 13	707.2	707.8	709.2	708.2	512.7	515.9
Laboratory 14	714.3	716.7	711.6	709.8	526.0	530.0
Laboratory 15	714.8	694.4	709.0	716.5	535.5	528.8
Laboratory 16	700.5	702.0	701.4	700.1	527.2	523.6
Laboratory 17	697.4	690.9	704.9	710.8	534.4	536.2

Table 3 Results

	Metribuzin SC 480 (414 g/kg Metribuzin)		Metribuzin 42 % SC	
	Day 1	Day 2	Day 1	Day 2
Laboratory 1	417.2	415.6	434.0	433.3
Laboratory 2	414.9	415.3	433.7	432.5
Laboratory 3	418.6	416.3	434.4	434.2
Laboratory 4	400.9	401.5	423.0	423.6
Laboratory 5	411.6	411.6	429.9	432.3
Laboratory 6	414.1	416.2	436.8	435.4
Laboratory 7	401.4	417.4	420.8	440.0
Laboratory 8	415.6	408.9	437.2	429.7
Laboratory 9	422.1	433.0	440.8	449.5
Laboratory 10	416.4	413.3	433.9	431.6
Laboratory 11	414.1	413.6	435.5	438.9
Laboratory 12	417.5	417.4	418.5	416.3
Laboratory 13	410.8	414.6	420.4	422.0
Laboratory 14	409.2	406.3	427.1	431.2
Laboratory 15	415.8	415.8	436.1	434.4
Laboratory 16	411.6	410.5	412.3	410.4
Laboratory 17	428.4	433.1	402.3	407.5

Table 4 Mean values

	Metribuzin TC_1	Metribuzin TC_2	Metribuzin WG 70	Metribuzin 70 % WG
Laboratory 1	962.3	992.0	675.8	709.8
Laboratory 2	964.6	995.1	688.4	712.6
Laboratory 3	971.4	1000.0	690.1	711.3
Laboratory 4	931.1	976.3	640.4	699.7
Laboratory 5	964.2	993.2	687.0	709.4
Laboratory 6	961.6	990.0	685.4	710.8
Laboratory 7	942.7	959.5	652.1	703.7
Laboratory 8	958.7	990.7	688.9	707.7
Laboratory 9	973.0	994.7	694.9	721.1
Laboratory 10	961.2	988.3	685.8	707.6
Laboratory 11	965.1	984.9	690.7	707.0
Laboratory 12	975.9	973.6	679.6	699.5
Laboratory 13	945.7	972.3	673.0	714.7
Laboratory 14	967.2	1006.1	698.1	723.3
Laboratory 15	961.6	987.0	689.7	716.9
Laboratory 16	972.4	971.3	701.4	701.2
Laboratory 17	968.5	971.4	704.4	702.9

Table 5 Mean values

	Metribuzin WP 70	Metribuzin 70 % WP	Metribuzin SC 600 (522 g/kg Metribuzin)
Laboratory 1	708.9	708.8	534.2
Laboratory 2	712.7	714.1	530.3
Laboratory 3	714.3	711.7	535.5
Laboratory 4	682.8	695.4	514.4
Laboratory 5	709.9	708.6	527.6
Laboratory 6	711.7	709.0	530.2
Laboratory 7	702.1	702.3	529.1
Laboratory 8	710.8	713.1	528.2
Laboratory 9	724.1	720.6	543.6
Laboratory 10	709.3	710.2	532.4
Laboratory 11	707.5	701.4	531.8
Laboratory 12	700.2	696.3	524.9
Laboratory 13	705.0	708.7	514.3
Laboratory 14	715.5	710.7	528.0
Laboratory 15	704.6	712.8	532.2
Laboratory 16	701.3	700.8	525.4
Laboratory 17	694.2	707.9	535.3

Table 6 Mean values

	Metribuzin SC 480 (414 g/kg Metribuzin)	Metribuzin 42 % SC
Laboratory 1	416.4	433.7
Laboratory 2	417.6	433.1
Laboratory 3	417.5	434.3
Laboratory 4	401.2	423.3
Laboratory 5	411.6	431.1
Laboratory 6	415.2	436.1
Laboratory 7	409.4	430.4
Laboratory 8	412.3	433.5
Laboratory 9	427.6	445.2
Laboratory 10	414.9	432.8
Laboratory 11	412.9	437.2
Laboratory 12	417.5	417.4
Laboratory 13	412.7	421.2
Laboratory 14	407.8	429.2
Laboratory 15	415.8	435.3
Laboratory 16	411.1	411.4
Laboratory 17	430.8	404.9

Table 7 Summary of the statistical evaluation (all data included)

	Metribuzin TC_1	Metribuzin TC_2	Metribuzin WG 70	Metribuzin 70 % WG
x_m [g/kg]	961.57	985.07	683.84	709.35
x_m [% w/w]	96.16	98.51	68.38	70.94
L	17	17	17	17
s_r	6.15	8.24	7.97	3.99
s_R	12.51	13.66	17.39	7.52
r	17.22	23.07	22.32	11.17
R	35.02	38.26	48.69	21.04
RSD _R	1.30	1.39	2.54	1.06
RSD _{R (Hor)}	2.01	2.00	2.12	2.11
HorRat	0.65	0.70	1.20	0.50

Table 8 Summary of the statistical evaluation (all data included)

	Metribuzin WP 70	Metribuzin 70 % WP	Metribuzin SC 600 (522 g/kg Metribuzin)
x_m [g/kg]	706.74	707.77	529.25
x_m [% w/w]	70.67	70.78	52.93
L	17	17	17
s_r	5.80	4.58	4.81
s_R	10.10	7.35	7.90
r	16.23	12.83	13.47
R	28.28	20.58	22.13
RSD _R	1.43	1.04	1.49
RSD _{R (Hor)}	2.11	2.11	2.20
HorRat	0.68	0.49	0.68

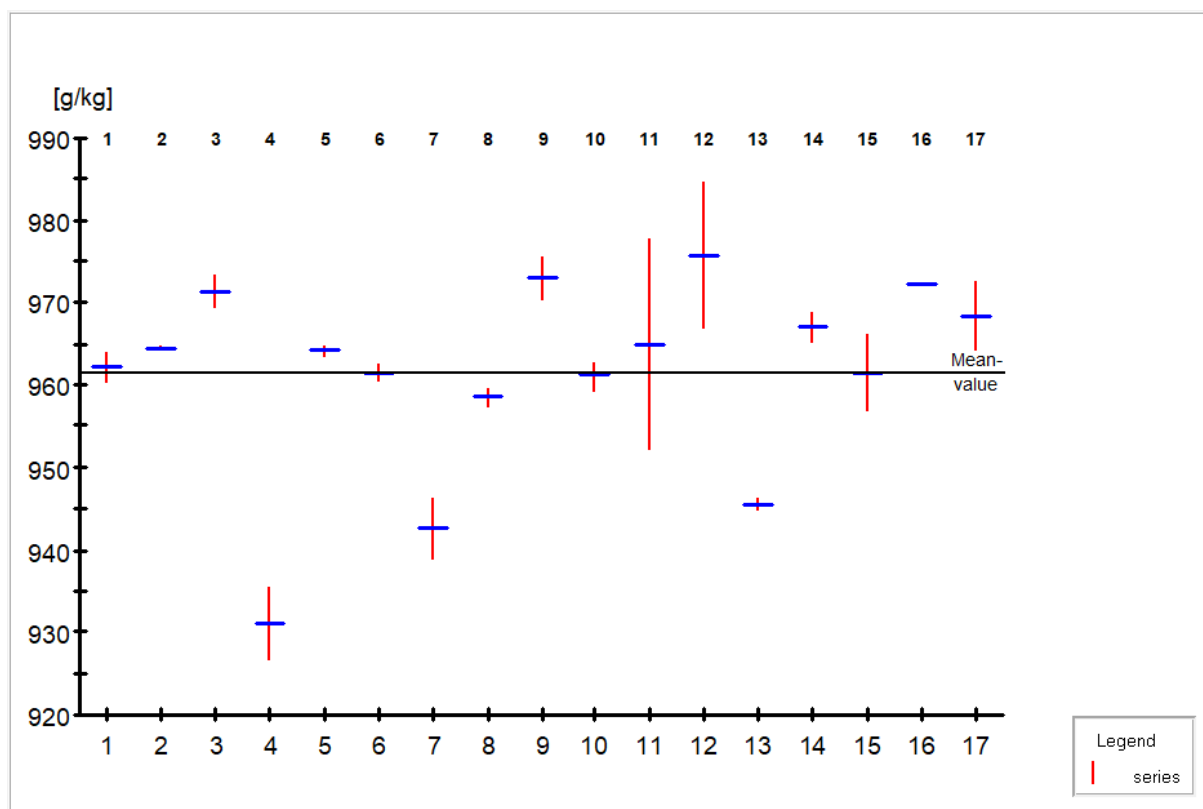
Table 9 Summary of the statistical evaluation (all data included)

	Metribuzin SC 480 (414 g/kg Metribuzin)	Metribuzin 42 % SC
x_m [g/kg]	414.87	428.81
x_m [% w/w]	41.49	42.88
L	17	17
s_r	3.87	4.15
s_R	7.34	10.55
r	10.84	11.62
R	20.56	29.55
RSD_R	1.77	2.46
$RSD_{R(Hor)}$	2.28	2.27
HorRat	0.78	1.08

x_m = total mean value
L = number of laboratories
 s_r = repeatability standard deviation
 s_R = reproducibility standard deviation
r = repeatability limit
R = reproducibility limit
 RSD_R = relative standard deviation of reproducibility
 $RSD_{R(Hor)}$ = Horwitz Value according to Horwitz equation
HorRat = Horwitz Ratio ($RSD_R / RSD_{R(Hor)}$)

Full set of 17 participants:

Fig. 1 Metribuzin tech. sample – 1 (Metribuzin TC_1)



Mean value: **961.57 g/kg**

Sr: **6.15**

sR: **12.51**

RSD_R: **1.30**

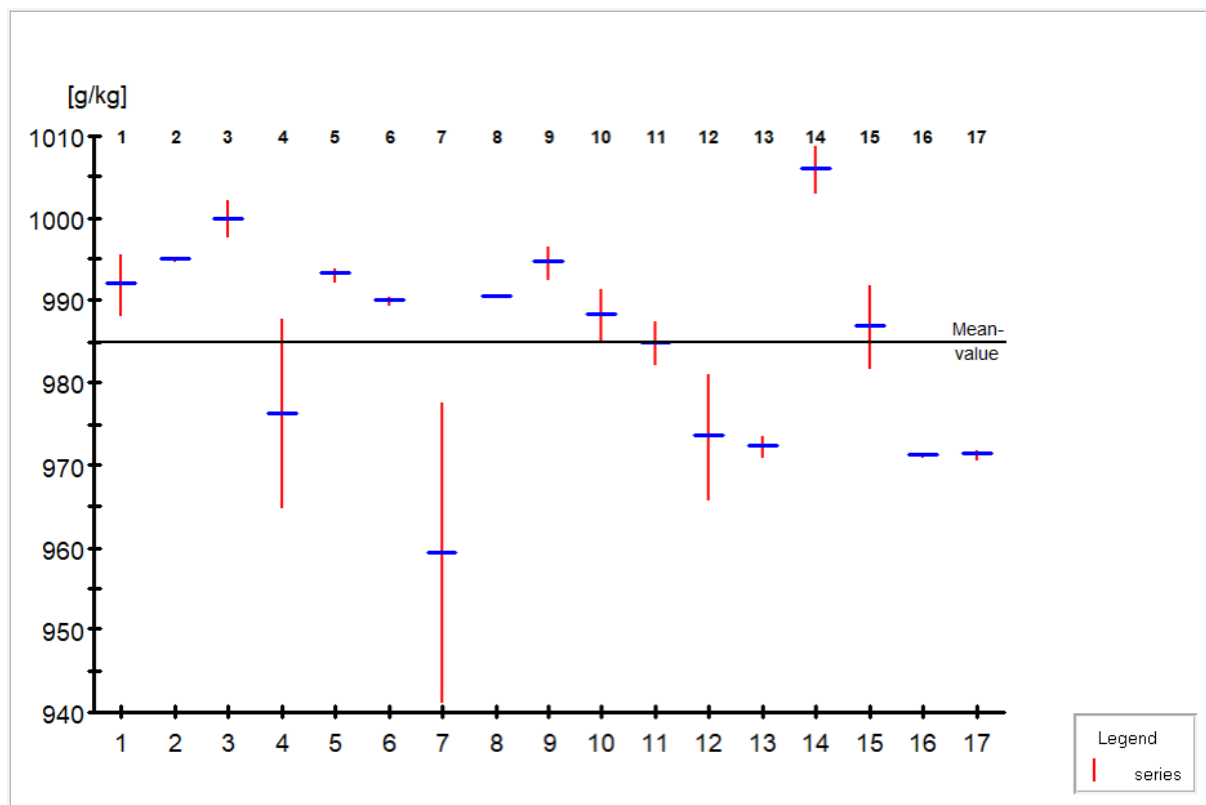
RSD_{R (Hor)}: **2.01**

HorRat: **0.65**

Outlier (Grubbs): **none**

Straggler (Grubbs) **lower (lab 4)**

Fig. 2 Metribuzin tech. sample – 2 (Metribuzin TC_2)



Mean value: **985.07 g/kg**

Sr: **8.24**

SR: **13.66**

RSD_R: **1.39**

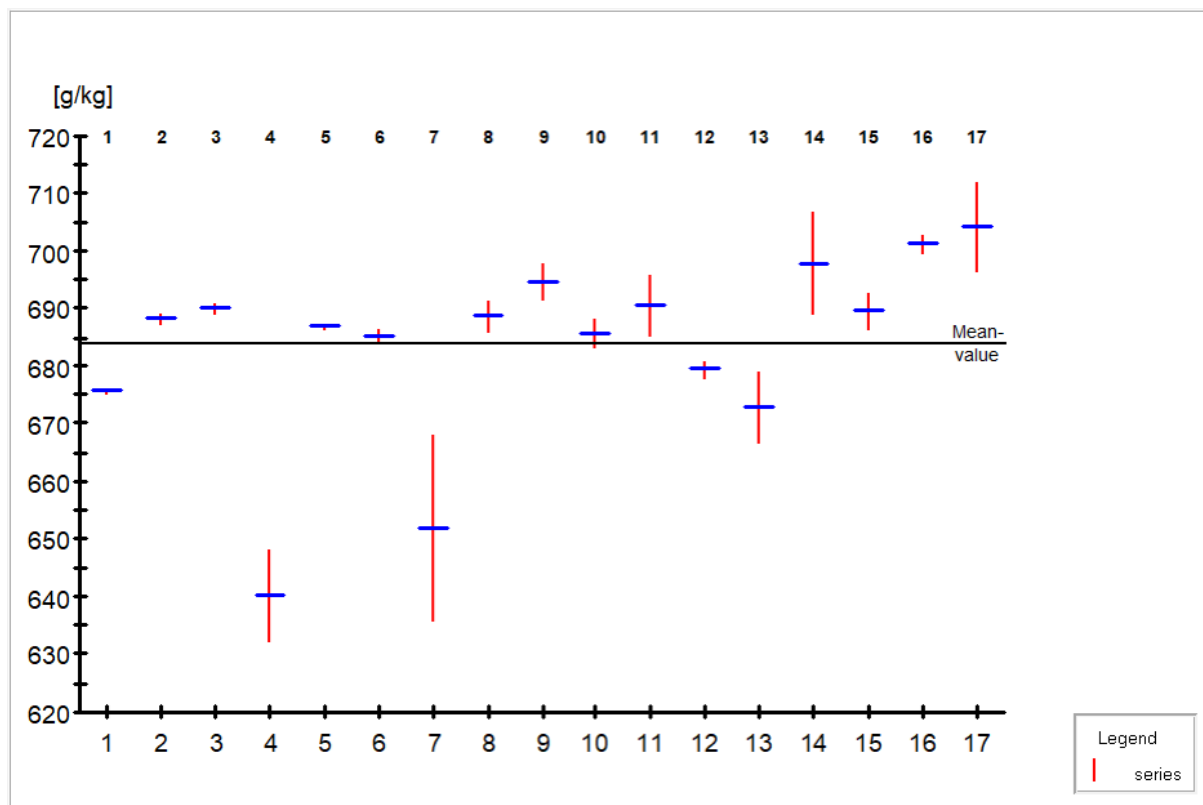
RSD_{R (Hor)}: **2.00**

HorRat: **0.70**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 3 Metribuzin WG 70 – 1 (Metribuzin WG 70)



Mean value: **683.84 g/kg**

Sr: **7.97**

sR: **17.39**

RSD_R: **2.54**

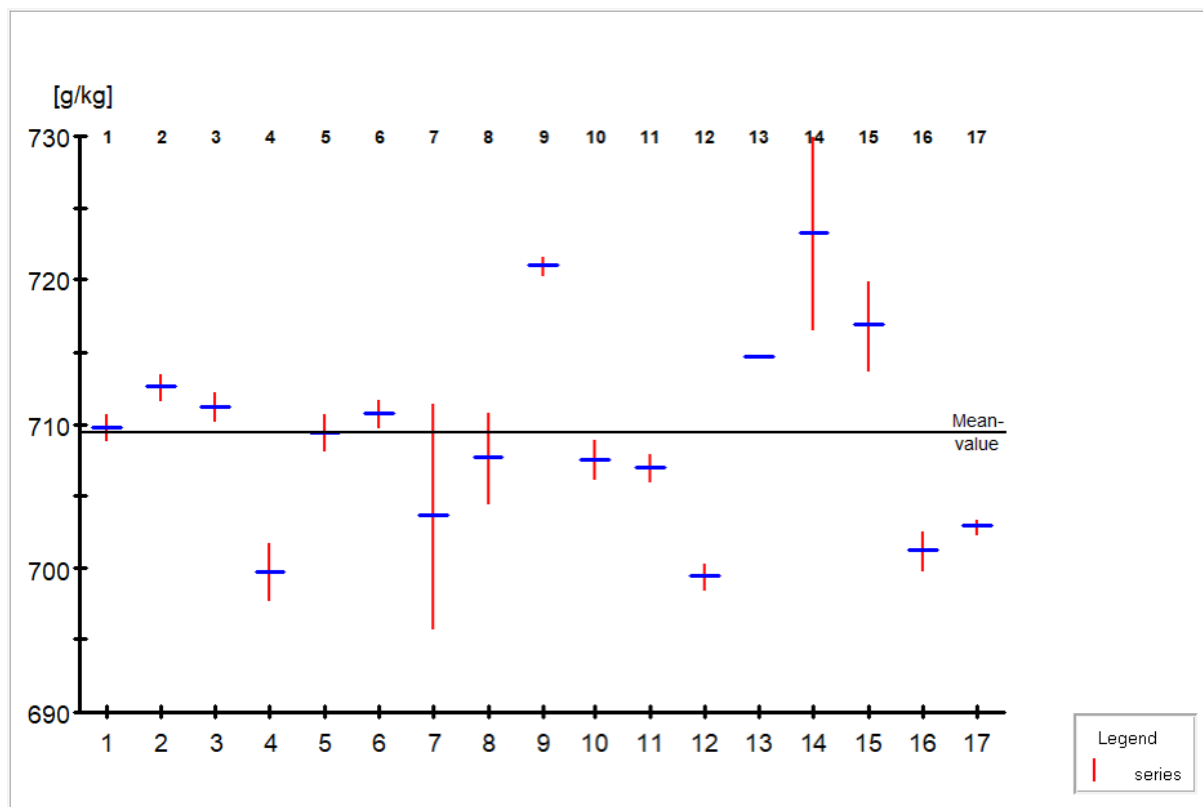
RSD_{R (Hor)}: **2.12**

HorRat: **1.20**

Outlier (Grubbs): **none**

Straggler (Grubbs) **lower (lab 4)**

Fig. 4 Metribuzin WG 70 – 2 (Metribuzin 70 % WG)



Mean value: **709.35 g/kg**

Sr: **3.99**

S_R: **7.52**

RSD_R: **1.06**

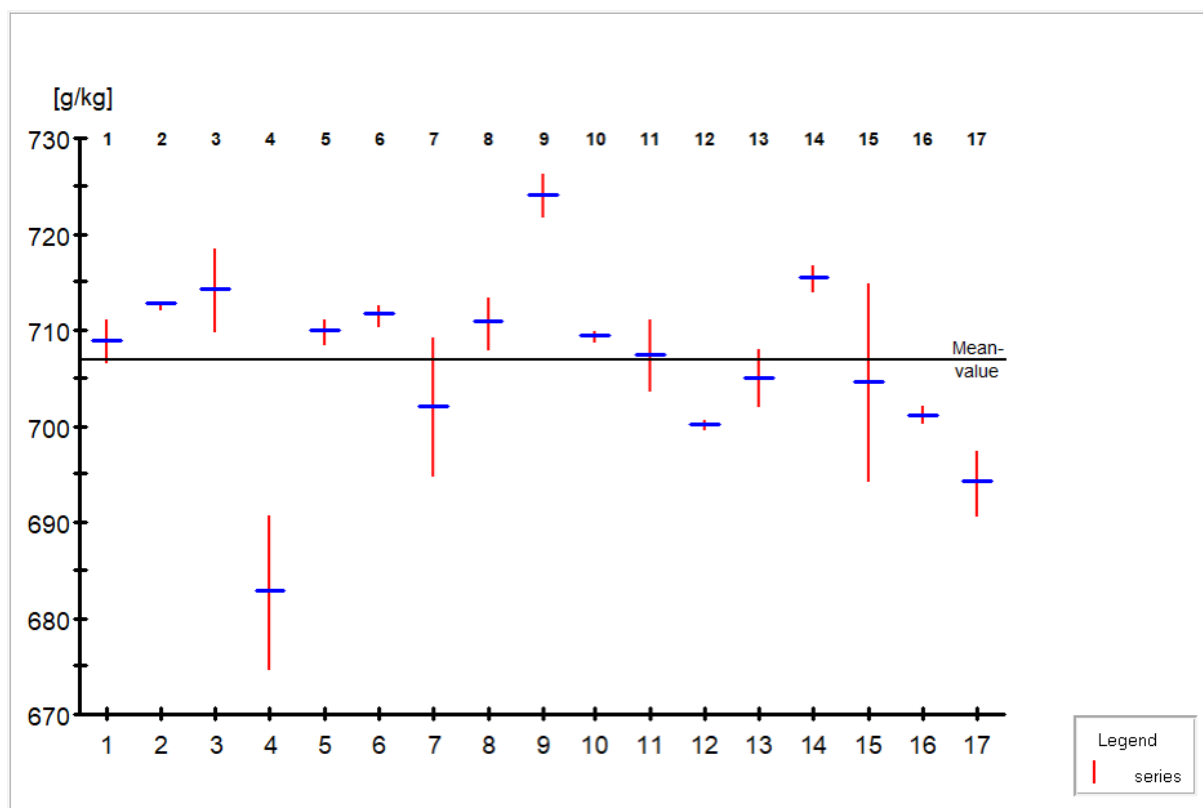
RSD_{R (Hor)}: **2.11**

HorRat: **0.50**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 5 Metribuzin WP 70 – 1 (Metribuzin WP 70)



Mean value: **706.74 g/kg**

Sr: **5.80**

S_R: **10.10**

RSD_R: **1.43**

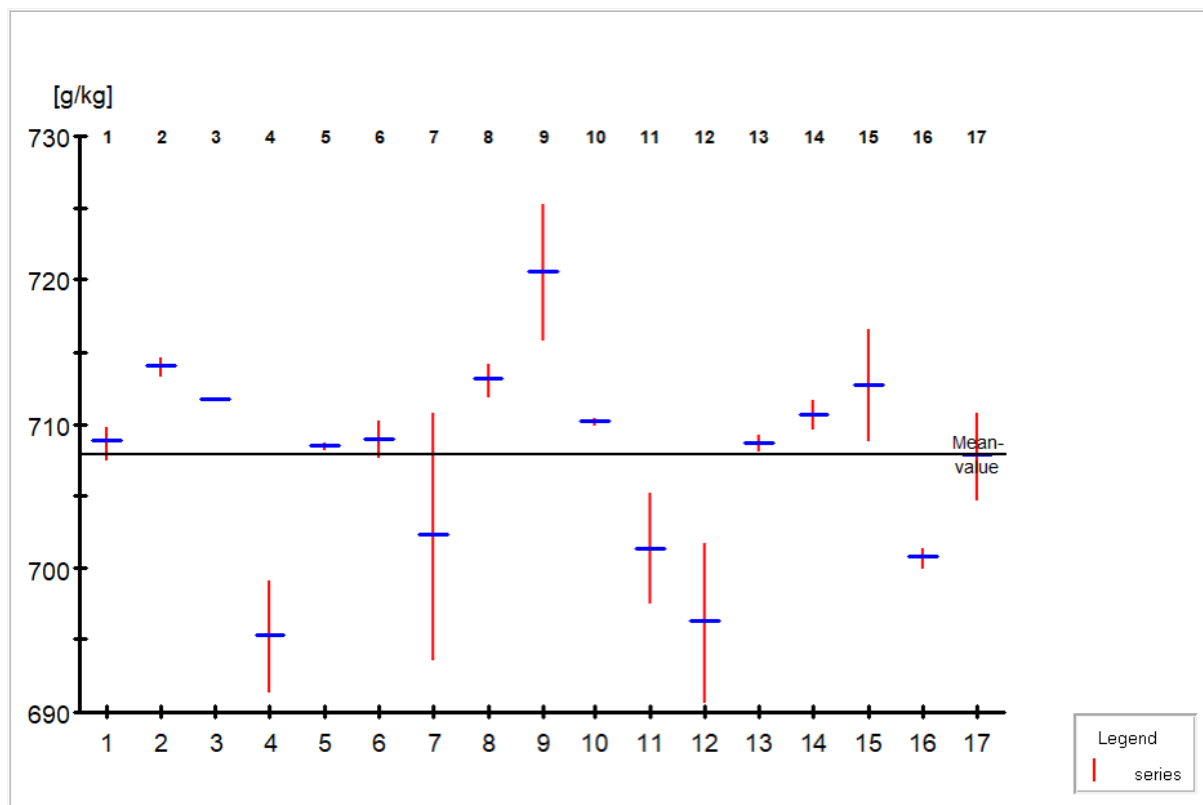
RSD_{R (Hor)}: **2.11**

HorRat: **0.68**

Outlier (Grubbs): **none**

Straggler (Grubbs) **lower (lab 4)**

Fig. 6 Metribuzin WP 70 – 2 (Metribuzin 70 % WP)



Mean value: **707.77 g/kg**

Sr: **4.58**

sR: **7.35**

RSD_R: **1.04**

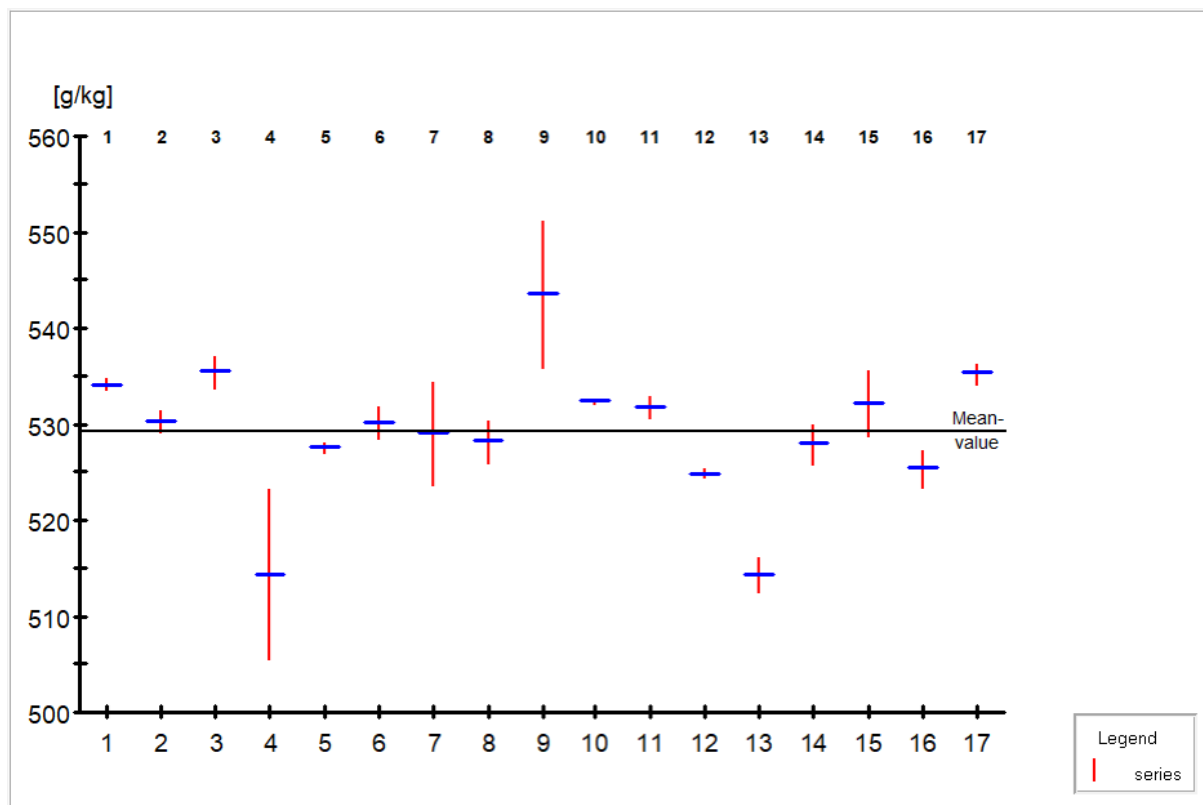
RSD_{R (Hor)}: **2.11**

HorRat: **0.49**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 7 Metribuzin SC 600; 522 g/kg Metribuzin (Metribuzin SC 600)



Mean value: **529.25 g/kg**

Sr: **4.81**

S_R: **7.90**

RSD_R: **1.49**

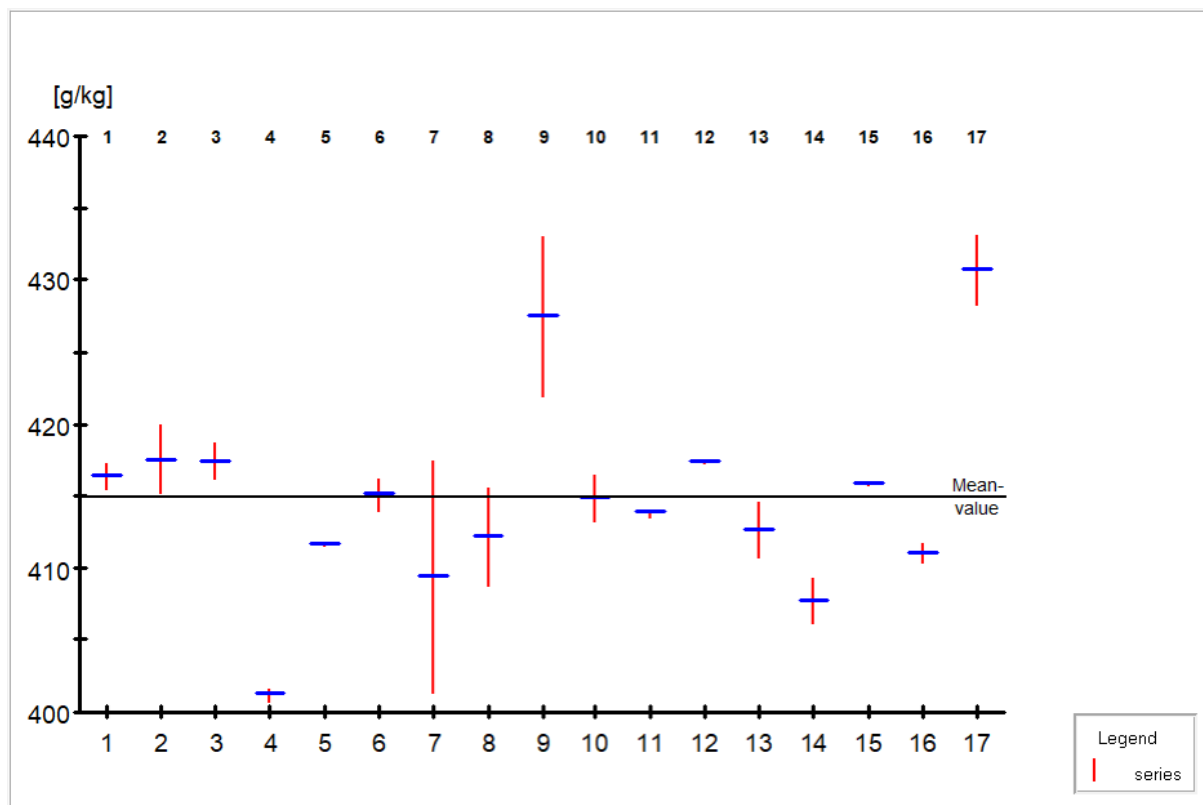
RSD_{R (Hor)}: **2.20**

HorRat: **0.68**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 8 Metribuzin SC 480 – 1; 414 g/kg Metribuzin (Metribuzin SC 480)



Mean value: **414.87 g/kg**

S_r: **3.87**

S_R: **7.34**

RSD_R: **1.77**

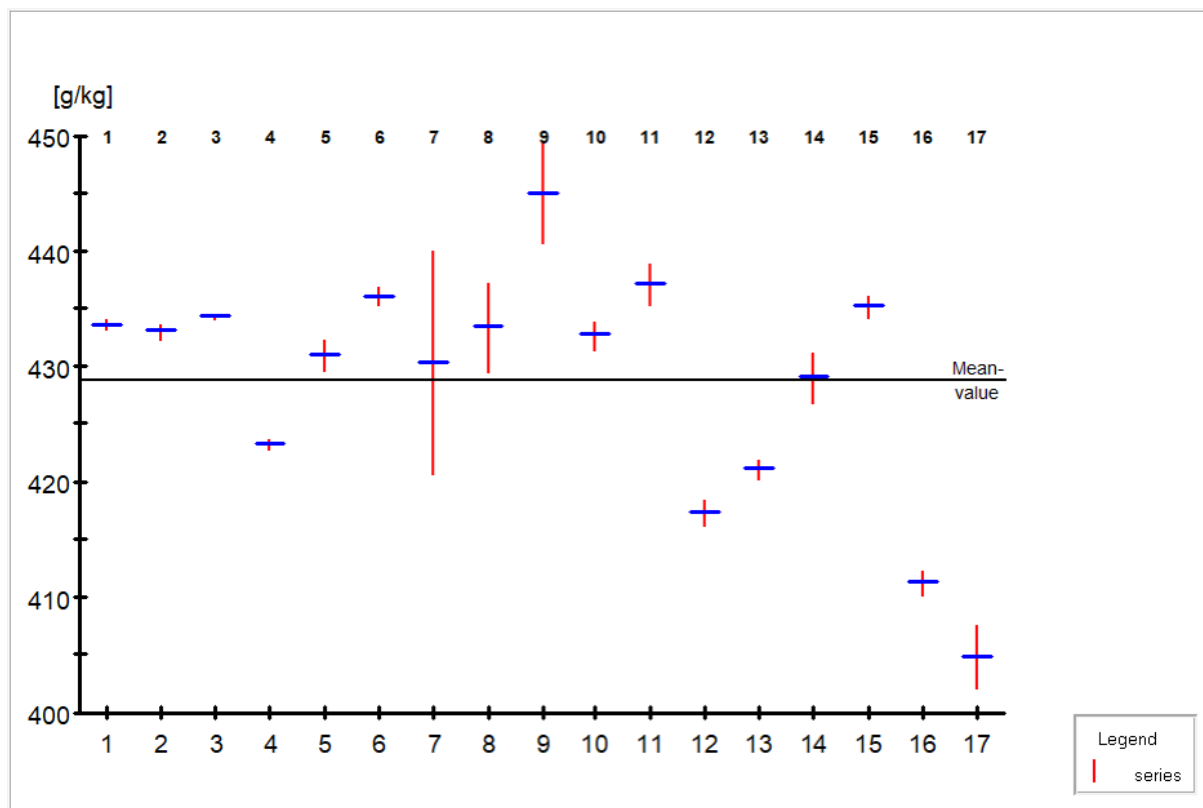
RSD_{R (Hor)}: **2.28**

HorRat: **0.78**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 9 Metribuzin SC 480 – 2 (Metribuzin 42 % SC)



Mean value: **428.81 g/kg**

Sr: **4.15**

sR: **10.55**

RSD_R: **2.46**

RSD_{R (Hor)}: **2.27**

HorRat: **1.08**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Determination of Metribuzin – elimination of labs who changed carrier gas (Hydrogen or Nitrogen instead of Helium, results of 11 laboratories)

All results are given in g/kg

Table 10 Results

	Metribuzin TC_1		Metribuzin TC_2		Metribuzin WG 70		Metribuzin 70 % WG	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Laboratory 1	963.9	960.6	995.5	988.4	676.0	675.6	710.6	709.0
Laboratory 2	964.6	964.5	995.0	995.1	687.6	689.1	713.4	711.7
Laboratory 3	969.6	973.2	1002.1	997.9	690.9	689.3	712.2	710.3
Laboratory 5	964.7	963.6	993.9	992.5	686.5	687.5	708.2	710.6
Laboratory 6	960.8	962.4	989.6	990.4	684.5	686.3	710.0	711.6
Laboratory 7	946.2	939.2	977.5	941.5	668.0	636.2	695.9	711.4
Laboratory 8	957.7	959.6	990.7	990.6	691.4	686.4	710.8	704.6
Laboratory 9	970.5	975.4	996.5	992.9	692.0	697.8	720.5	721.6
Laboratory 12	967.1	984.6	966.1	981.1	680.8	678.3	698.6	700.3
Laboratory 15	966.1	957.0	991.9	982.0	692.6	686.8	713.9	719.9
Laboratory 16	972.4	972.4	971.1	971.5	699.9	702.8	702.5	699.9

Table 11 Results

	Metribuzin WP 70		Metribuzin 70 % WP		Metribuzin SC 600 (522 g/kg Metribuzin)	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Laboratory 1	711.0	706.8	709.8	707.7	533.6	534.8
Laboratory 2	712.9	712.4	714.6	713.5	531.4	529.2
Laboratory 3	718.5	710.0	711.7	711.7	537.0	534.0
Laboratory 5	708.8	711.0	708.4	708.7	527.1	528.1
Laboratory 6	710.7	712.6	707.8	710.2	528.6	531.8
Laboratory 7	695.0	709.2	693.8	710.8	523.8	534.4
Laboratory 8	713.3	708.2	712.1	714.1	530.3	526.1
Laboratory 9	721.9	726.2	716.0	725.2	536.0	551.1
Laboratory 12	699.9	700.5	701.7	690.9	525.2	524.6
Laboratory 15	714.8	694.4	709.0	716.5	535.5	528.8
Laboratory 16	700.5	702.0	701.4	700.1	527.2	523.6

Table 12 Results

	Metribuzin SC 480 (414 g/kg Metribuzin)		Metribuzin 42 % SC	
	Day 1	Day 2	Day 1	Day 2
Laboratory 1	417.2	415.6	434.0	433.3
Laboratory 2	414.9	415.3	433.7	432.5
Laboratory 3	418.6	416.3	434.4	434.2
Laboratory 5	411.6	411.6	429.9	432.3
Laboratory 6	414.1	416.2	436.8	435.4
Laboratory 7	401.4	417.4	420.8	440.0
Laboratory 8	415.6	408.9	437.2	429.7
Laboratory 9	422.1	433.0	440.8	449.5
Laboratory 12	417.5	417.4	418.5	416.3
Laboratory 15	415.8	415.8	436.1	434.4
Laboratory 16	411.6	410.5	412.3	410.4

Table 13 Mean values

	Metribuzin TC_1	Metribuzin TC_2	Metribuzin WG 70	Metribuzin 70 % WG
Laboratory 1	962.3	992.0	675.8	709.8
Laboratory 2	964.6	995.1	688.4	712.6
Laboratory 3	971.4	1000.0	690.1	711.3
Laboratory 5	964.2	993.2	687.0	709.4
Laboratory 6	961.6	990.0	685.4	710.8
Laboratory 7	942.7	959.5	652.1	703.7
Laboratory 8	958.7	990.7	688.9	707.7
Laboratory 9	973.0	994.7	694.9	721.1
Laboratory 12	975.9	973.6	679.6	699.5
Laboratory 15	961.6	987.0	689.7	716.9
Laboratory 16	972.4	971.3	701.4	701.2

Table 14 Mean values

	Metribuzin WP 70	Metribuzin 70 % WP	Metribuzin SC 600 (522 g/kg Metribuzin)
Laboratory 1	708.9	708.8	534.2
Laboratory 2	712.7	714.1	530.3
Laboratory 3	714.3	711.7	535.5
Laboratory 5	709.9	708.6	527.6
Laboratory 6	711.7	709.0	530.2
Laboratory 7	702.1	702.3	529.1
Laboratory 8	710.8	713.1	528.2
Laboratory 9	724.1	720.6	543.6
Laboratory 12	700.2	696.3	524.9
Laboratory 15	704.6	712.8	532.2
Laboratory 16	701.3	700.8	525.4

Table 15 Mean values

	Metribuzin SC 480 (414 g/kg Metribuzin)	Metribuzin 42 % SC
Laboratory 1	416.4	433.7
Laboratory 2	417.6	433.1
Laboratory 3	417.5	434.3
Laboratory 5	411.6	431.1
Laboratory 6	415.2	436.1
Laboratory 7	409.4	430.4
Laboratory 8	412.3	433.5
Laboratory 9	427.6	445.2
Laboratory 12	417.5	417.4
Laboratory 15	415.8	435.3
Laboratory 16	411.1	411.4

Table 16 Summary of the statistical evaluation (set of 11 laboratories)

	Metribuzin TC_1	Metribuzin TC_2	Metribuzin WG 70	Metribuzin 70 % WG
x_m [g/kg]	964.37	986.08	684.83	709.43
x_m [% w/w]	96.44	98.61	68.48	70.94
L	11	11	11	11
s_r	4.74	8.80	7.16	3.95
s_R	9.77	13.92	13.77	6.98
r	13.26	24.63	20.04	11.05
R	27.35	38.98	38.56	19.55
RSD _R	1.01	1.41	2.01	0.98
RSD _{R (Hor)}	2.01	2.00	2.12	2.11
HorRat	0.50	0.71	0.95	0.46

Table 17 Summary of the statistical evaluation (set of 11 laboratories)

	Metribuzin WP 70	Metribuzin 70 % WP	Metribuzin SC 600 (522 g/kg Metribuzin)
x_m [g/kg]	709.12	708.90	531.01
x_m [% w/w]	70.91	70.89	53.10
L	11	11	11
s_r	5.89	5.06	4.49
s_R	8.10	7.75	6.19
r	16.49	14.17	12.56
R	22.68	21.70	17.32
RSD_R	1.14	1.09	1.16
$RSD_{R(Hor)}$	2.11	2.11	2.20
HorRat	0.54	0.52	0.53

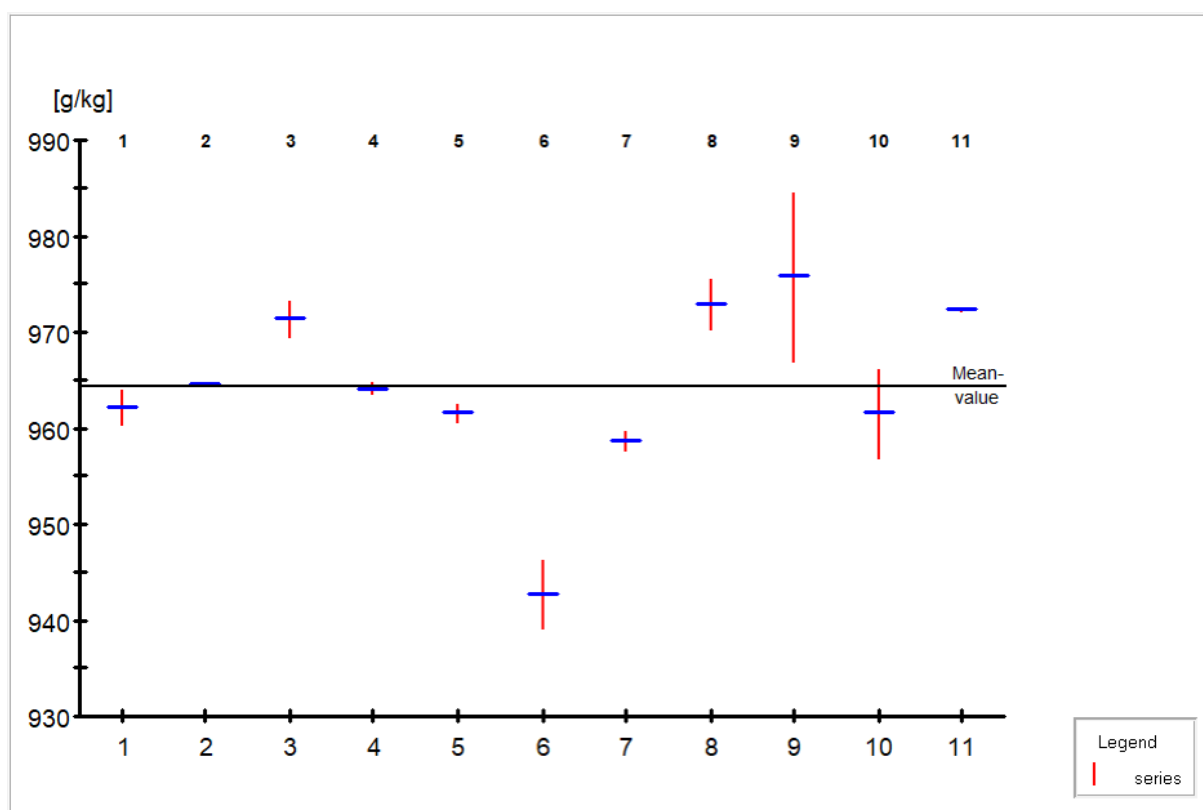
Table 18 Summary of the statistical evaluation (set of 11 laboratories)

	Metribuzin SC 480 (414 g/kg Metribuzin)	Metribuzin 42 % SC
x_m [g/kg]	415.61	431.02
x_m [% w/w]	41.56	43.10
L	11	11
s_r	4.54	4.87
s_R	5.87	9.81
r	12.72	13.63
R	16.43	27.47
RSD_R	1.41	2.28
$RSD_{R(Hor)}$	2.28	2.27
HorRat	0.62	1.00

X_m	=	total mean value
L	=	number of laboratories
s_r	=	repeatability standard deviation
S_R	=	reproducibility standard deviation
r	=	repeatability limit
R	=	reproducibility limit
RSD_R	=	relative standard deviation of reproducibility
$RSD_{R(Hor)}$	=	Horwitz Value according to Horwitz equation
HorRat	=	Horwitz Ratio ($RSD_R / RSD_{R(Hor)}$)

Set of 11 participants using Helium as carrier gas:

Fig. 10 Metribuzin tech. sample – 1 (Metribuzin TC_1)



Mean value: **964.37 g/kg**

s_r : **4.74**

S_R : **9.77**

RSD_R : **1.01**

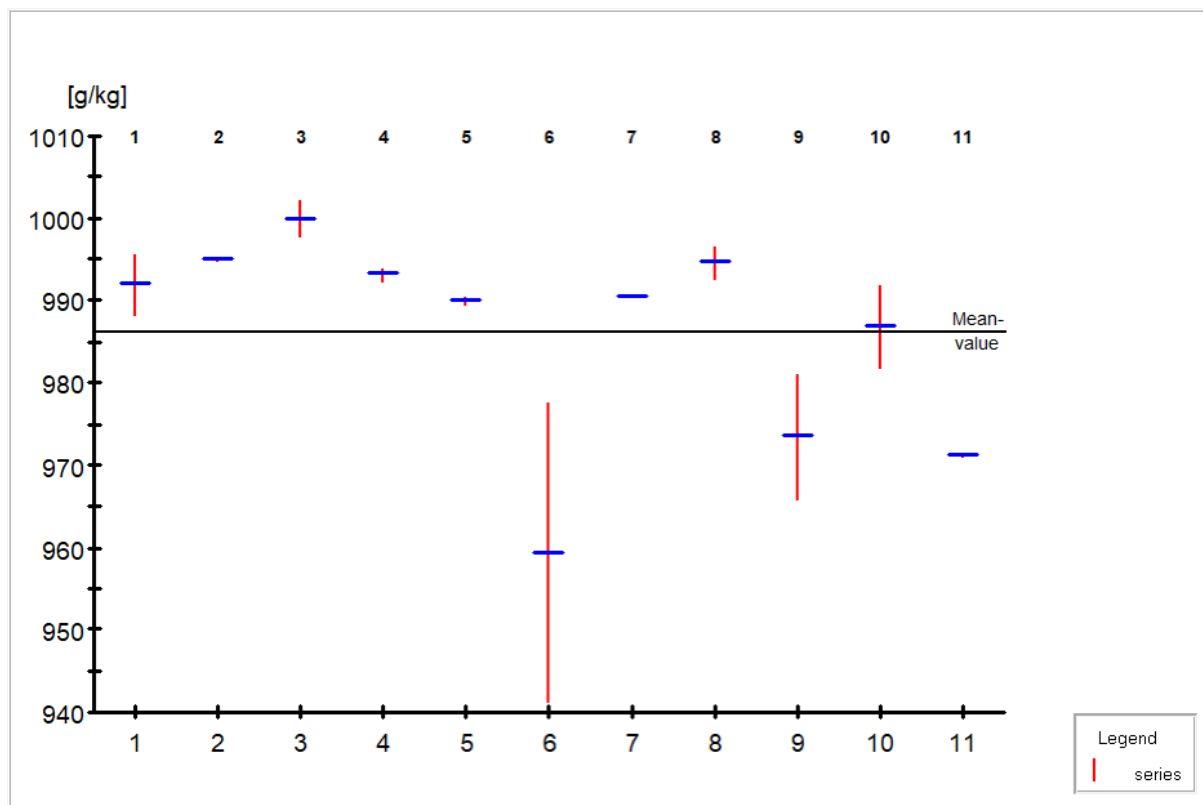
$RSD_{R(Hor)}$: **2.01**

HorRat: **0.50**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 11 Metribuzin tech. sample – 2 (Metribuzin TC_2)



Mean value: **986.08 g/kg**

Sr: **8.80**

SR: **13.92**

RSD_R: **1.41**

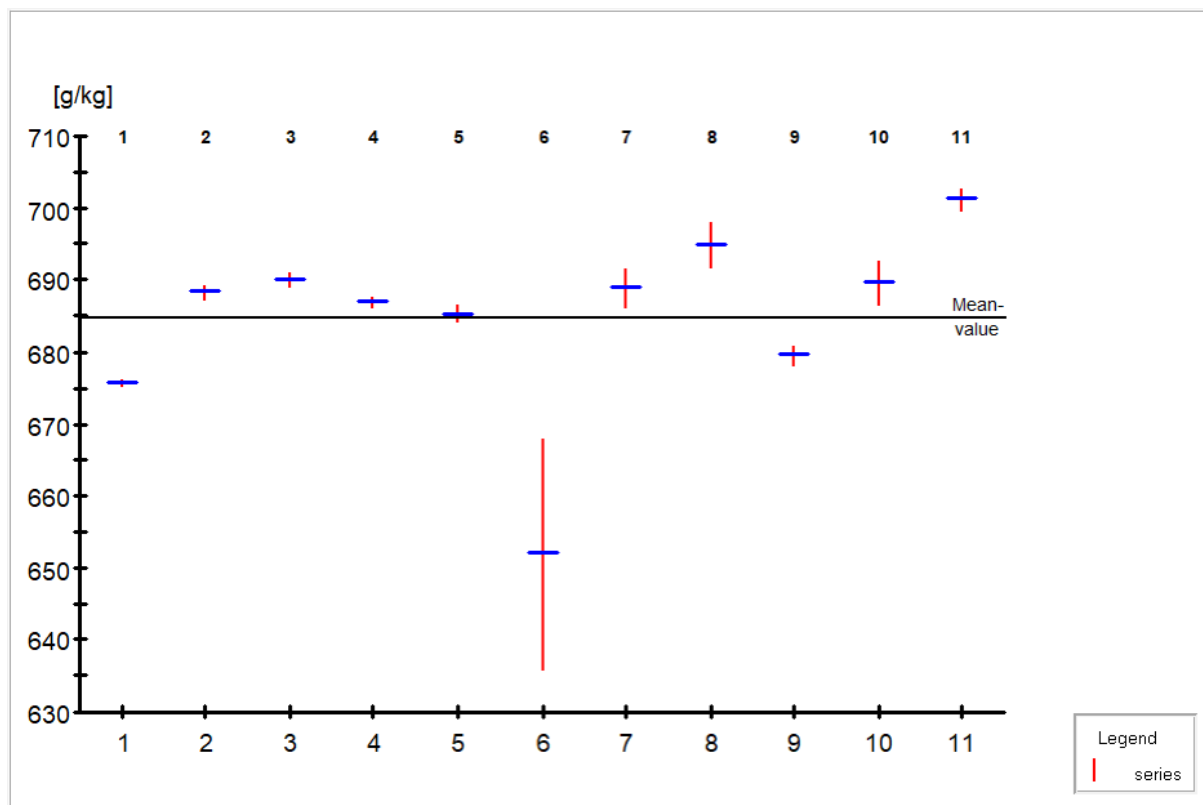
RSD_{R (Hor)}: **2.00**

HorRat: **0.71**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 12 Metribuzin WG 70 – 1 (Metribuzin WG 70)



Mean value: **684.83 g/kg**

Sr: **7.16**

SR: **13.77**

RSD_R: **2.01**

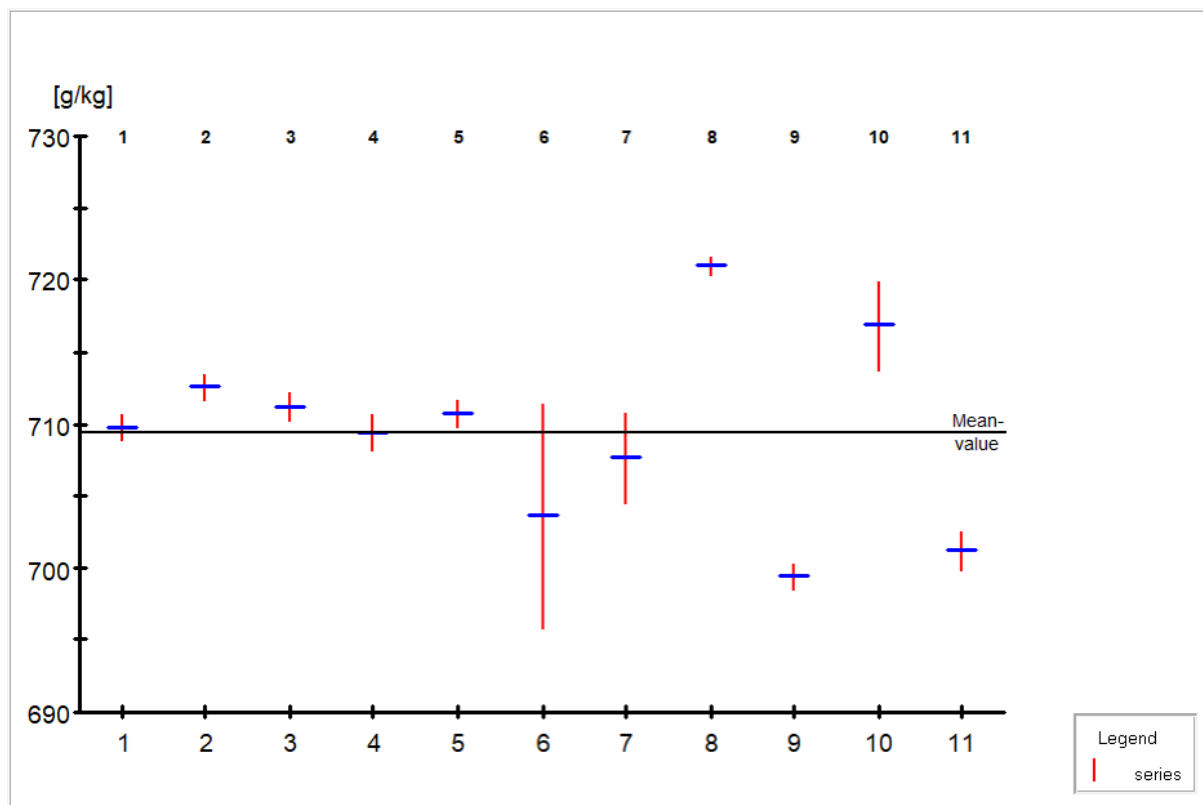
RSD_{R (Hor)}: **2.12**

HorRat: **0.95**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 13 Metribuzin WG 70 – 2 (Metribuzin 70 % WG)



Mean value: **709.43 g/kg**

Sr: **3.95**

SR: **6.98**

RSD_R: **0.98**

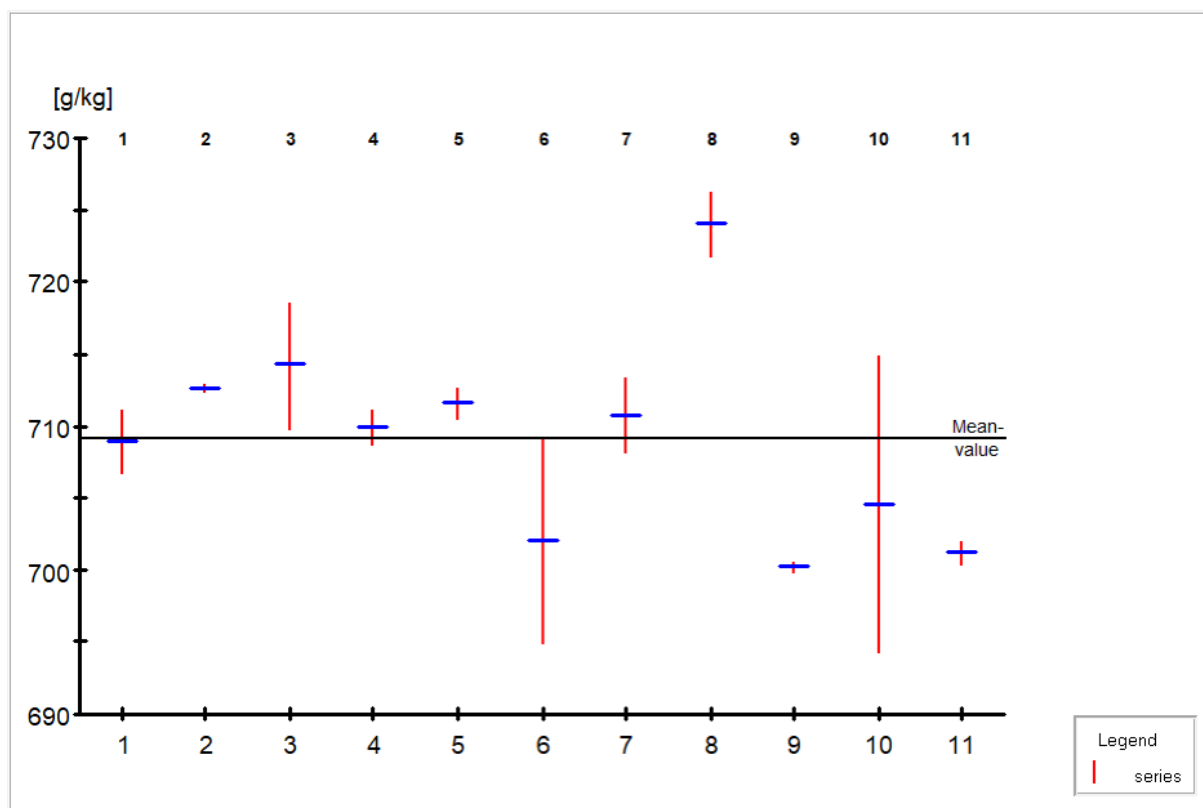
RSD_{R (Hor)}: **2.11**

HorRat: **0.46**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 14 Metribuzin WP 70 – 1 (Metribuzin WP 70)



Mean value: **709.12 g/kg**

Sr: **5.89**

S_R: **8.10**

RSD_R: **1.14**

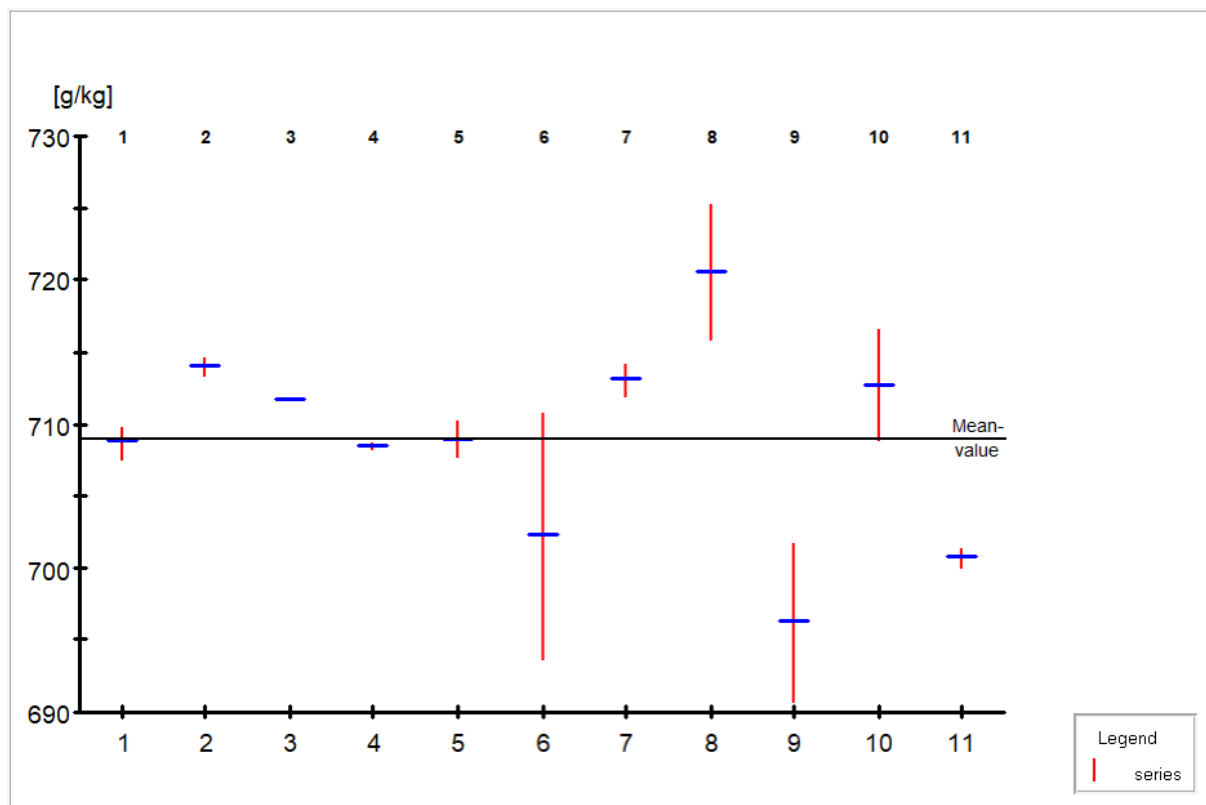
RSD_{R (Hor)}: **2.11**

HorRat: **0.54**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 15 Metribuzin WP 70 – 2 (Metribuzin 70 % WP)



Mean value: **708.90 g/kg**

Sr: **5.06**

Sr: **7.75**

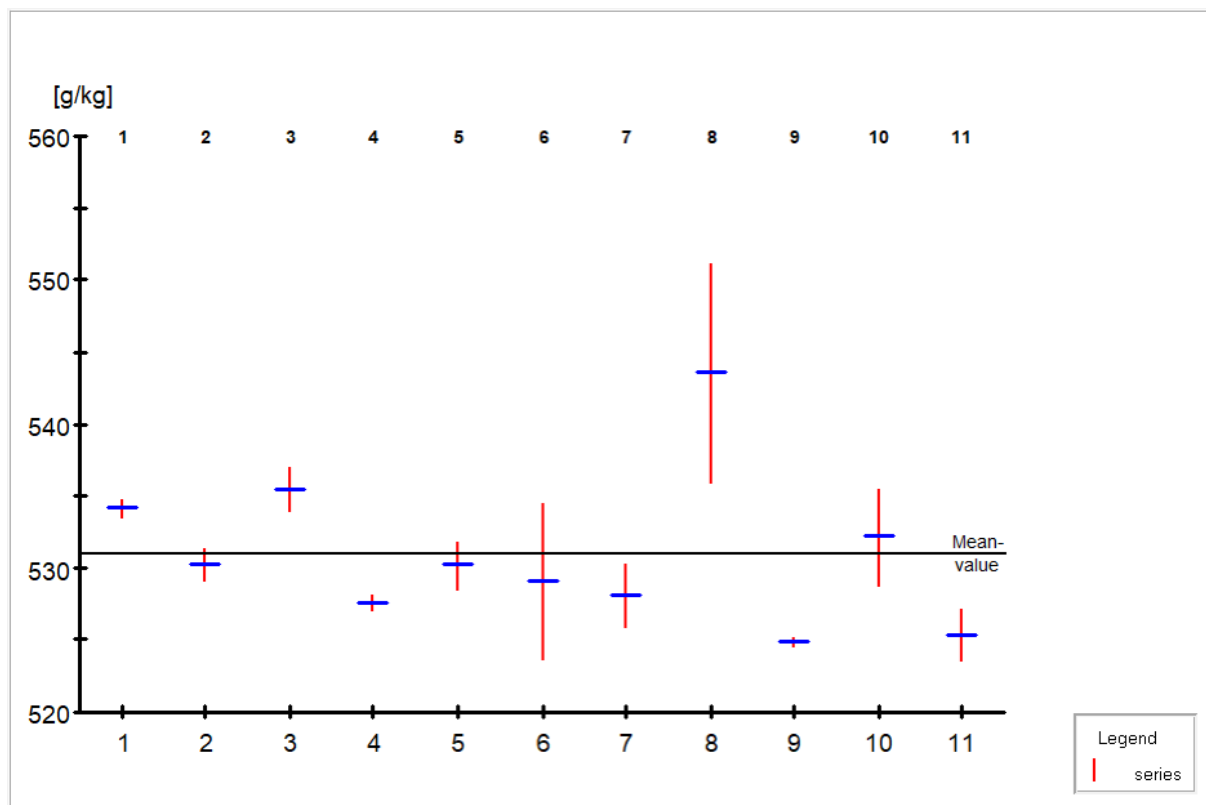
RSD_R: **1.09**

RSD_{R (Hor)}: **2.11**

HorRat: **0.52**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 16 Metribuzin SC 600; 522 g/kg Metribuzin (Metribuzin SC 600)

Mean value: **531.01 g/kg**

Sr: **4.49**

sR: **6.19**

RSD_R: **1.16**

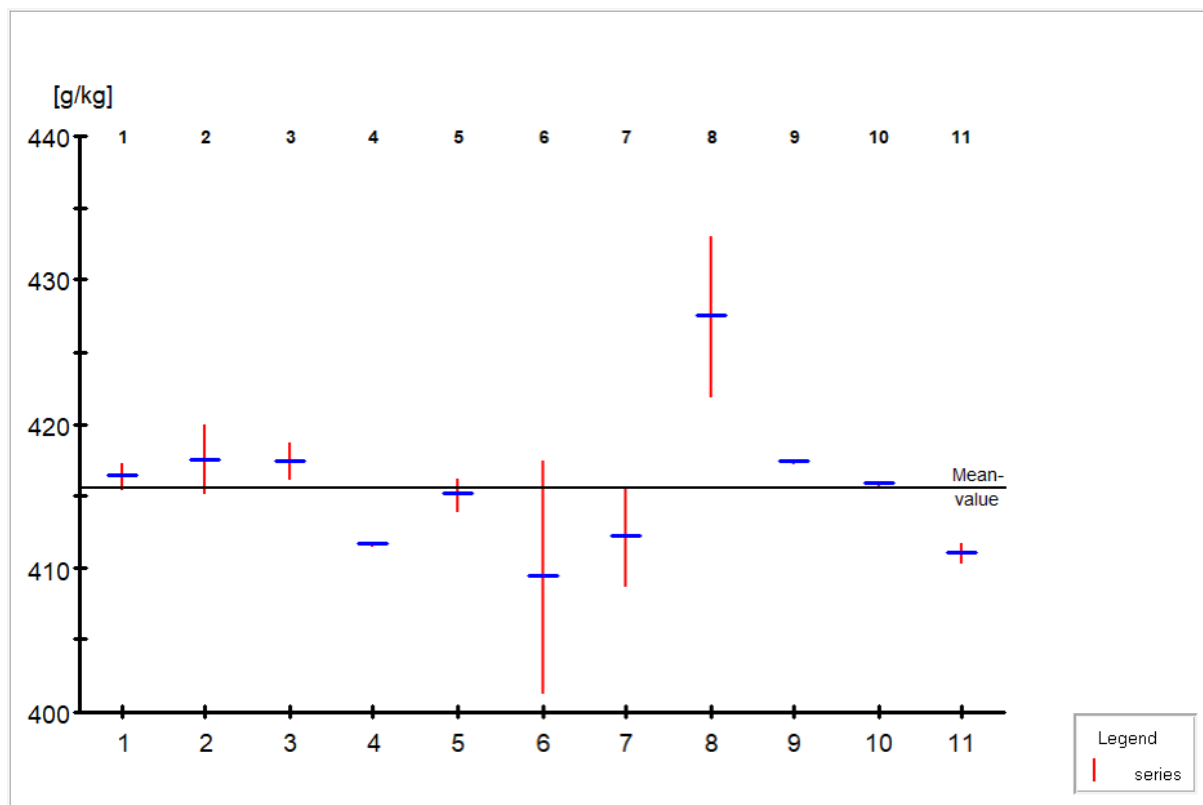
RSD_{R (Hor)}: **2.20**

HorRat: **0.53**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Fig. 17 Metribuzin SC 480 – 1; 414 g/kg Metribuzin (Metribuzin SC 480)



Mean value: **415.61 g/kg**

S_r: **4.54**

S_R: **5.87**

RSD_R: **1.41**

RSD_{R (Hor)}: **2.28**

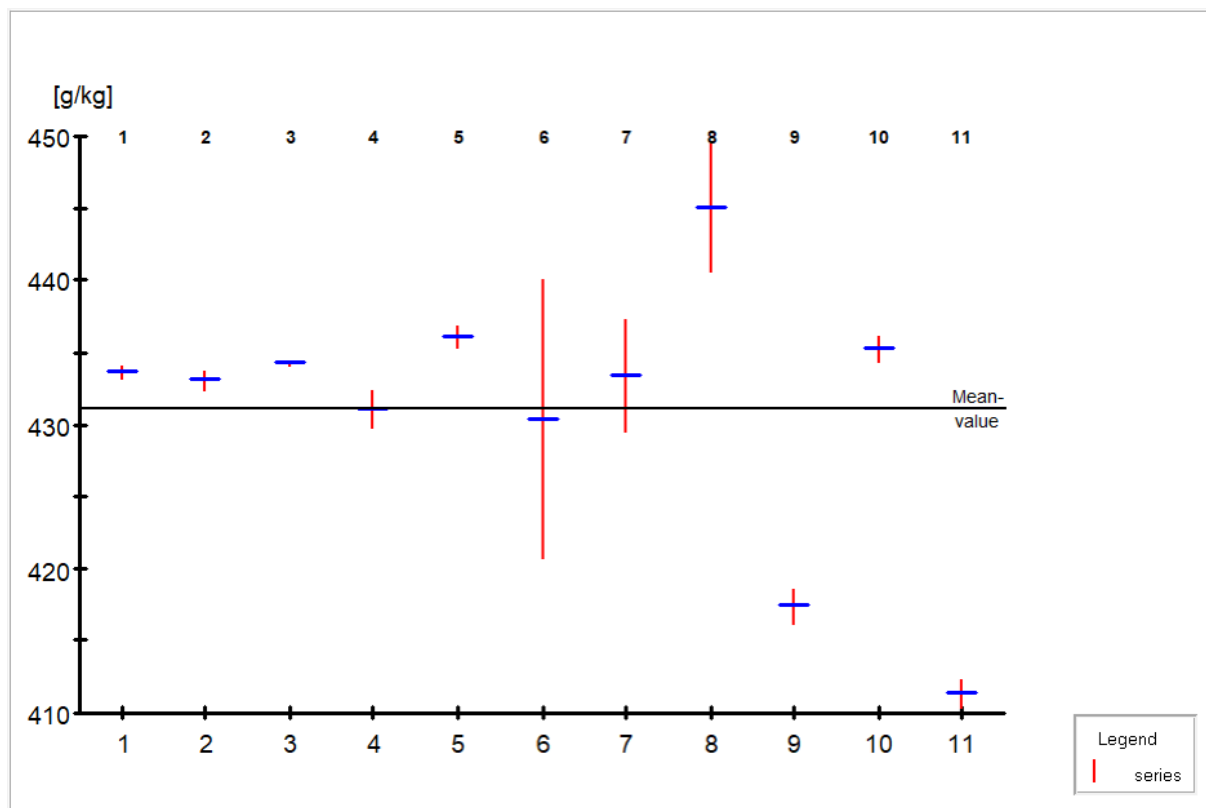
HorRat: **0.62**

Outlier (Grubbs): **none**

Straggler (Grubbs) **upper (lab 8)***

***refers to laboratory 9 in the list of all participants**

Fig. 18 Metribuzin SC 480 – 2 (Metribuzin 42 % SC)



Mean value: **431.02 g/kg**

Sr: **4.87**

sR: **9.81**

RSD_R: **2.28**

RSD_{R (Hor)}: **2.27**

HorRat: **1.00**

Outlier (Grubbs): **none**

Straggler (Grubbs) **none**

Table 19 Impact of the carrier gas onto the Horwitz Ratio (HorRat)

Sample	HorRat		
	full set of labs (17) ¹⁾	reduced set (11) ²⁾	Δ
Metribuzin TC_1	0.65	0.50	0.15
Metribuzin TC_2	0.70	0.71	- 0.01
Metribuzin WG 70	1.20	0.95	0.25
Metribuzin 70 %WG	0.50	0.46	0.04
Metribuzin WP 70	0.68	0.54	0.14
Metribuzin 70 % WP	0.49	0.52	- 0.03
Metribuzin SC 600	0.68	0.53	0.15
Metribuzin SC 480	0.78	0.62	0.14
Metribuzin 42 % SC	1.08	1.00	0.08

1) Use of carrier gas Helium, Hydrogen and Nitrogen

2) Only use of carrier gas Helium (default)

7. Conclusions

A total of 17 different laboratories have participated in this full scale collaborative study. The statistical evaluation is reported on the one hand with 11 laboratories which used Helium as a carrier gas as described in the CIPAC method and on the other hand with the full set of participating laboratories. Six of the total 17 participants used Hydrogen or Nitrogen, respectively, in deviation of the original method.

The data presented in the statistical summary show that use of Helium as a carrier gas led to HorRat values all within the required range and gained significant improvements compared to full data set in most cases (table 19). However, even by carrier gas variation, 7 of 9 samples fulfilled the HorRat criterion, only two failed shortly. That is evidence for the fact that the present GC method is acceptable and robust even with respect to the carrier gas type and therefore is suitable to produce reproducible results.

Bayer AG, Crop Science Division and Jiangsu Seven Continent consider this method to be suitable for the intended purpose, without further changes, and recommend accepting it as a provisional CIPAC method for the determination of Metribuzin in technical grade material and in SC, WG and WP formulations.