REPORT 4832/R

CIPAC FULL SCALE COLLABORATIVE STUDY ON THE DETERMINATION OF FLAZASULFURON IN FLAZASULFURON TECHNICAL MATERIAL AND FORMULATED PRODUCT BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Progress Report to CIPAC on Method Development Work
Conducted by the ISK Company

By

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1 INTRODUCTION

The results of CIPAC full scale collaborative study for Flazasulfuron technical product and Flazasulfuron water dispersible granules are reported in this present study for its content of Flazasulfuron.

In October 2011, CIPAC Information Sheet No. 290 was sent out by the CIPAC Secretary inviting members to participate in a collaborative study to validate the high performance liquid chromatographic assay method for Flazasulfuron in technical material and formulated product. A copy of the analytical method, protocol for the performance of the study, analysis report forms, samples and standards required for the analysis were sent to the respondents. The participants who completed the study are listed in Section 1.2.

The analytical method assessed in this study took into consideration CIPAC comments made in the frame of two previous small scale collaborative trials (reports presented in June 2010 and 2011).

1.1 Samples

Five test samples, homogenized, and analytical standards were sent to the participants. All samples came from different batches of technical material and formulation.

Test Sample	**Identification Code**
Flazasulfuron Technical batch 028	Tech-1
Flazasulfuron Technical batch 029	Tech-2
Flazasulfuron 25 WG batch 23061	Flazasulfuron 25 WG-1
Flazasulfuron 25 WG batch 23062	Flazasulfuron 25 WG-2
Flazasulfuron 25 WG batch 23063	Flazasulfuron 25 WG-3

Flazasulfuron analytical standard (batch No. Y-920205, 100.0 % purity) was provided by ISK.

1.2 Participants

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Lab 4	Anne-Marie Dos Santos Alves	Syngenta Crop Protection Münchwillen Breitenloh 5 CH-4333 Münchwillen Switzerland
Lab 5	Xiangdong Shao	Nutrichem Laboratory Co., Ltd. D-1, Dongsheng Science Park, 66 Xixiaokou Road, Haidian District, Beijing 100192 P. R. China
Lab 6	Michael Haustein	CURRENTA GmbH & Co. OHG ANT Produktionsanalytik Building A 559 D-41538 Dormagen Germany
Lab 7	Luis Manso	Laboratorio Arbitral Agroalimentario Ministerio de Agricultura, Alimentación y Medio Ambiente Aguarón, 13. Aravaca. 28023 Madrid Spain
Lab 8	Lajos Benke	National Food Chain Safety Office, Directorate of Plant Protection Soil Conservation and Agri-environment, Pesticide Analytical Laboratory Ország út 23 H-2481 Velence Hungary
Lab 9	Dewi Lesmawaty	PT Agricon JL. Melati No.5 Desa Wanaherang Kec. Gunung Putri. Cibinong, 16965 Indonesia
Lab10	Jim Garvey	Pesticides Control Service Laboratory Department of Agriculture, Food and the Marine, Backweston Campus, Youngs Cross, Celbridge, Co. Kildare IRELAND

Lab 11	Angela Santilio	National Institute of Health – Department of Environmental and Primary Prevention V.le Regina Elena, 299 00161 ROME Italy
Lab 12	Krste Tashev	State Phytosanitary Laboratory Ministry of Agriculture, Forestry and Water Economy bul Aleksandar the Great bb, 1000 Skopje (SPL) Jurij Gagarin br. 15 1000 Skopje (MAFWE) REPUBLIC OF MACEDONIA
Lab 13	Florentina Nedelcu	Central Phytosanitary Laboratory 11 Voluntari St, Code 077190, Voluntari Romania
Lab 14	Ana Gregorčič	AGRICULTURAL INSTITUTE OF SLOVENIA (Kmetijski inštitut Slovenije) Hacquetova ulica 17, 1000 Ljubljana, SLOVENIJA
Lab 15	Juliana Schlosserova	Central Controlling and Testing Institute in Agriculture (ÚKSÚP) Hanulova 9/A, 844 29 Bratislava 42 Slovakia
Lab 16	Andrew Plumb	The Food and Environment Research Agency Sand Hutton, York, North Yorkshire YO41 1LZ, UK

2 ANALYTICAL METHOD

2.1 Scope

This method is applicable to the determination of Flazasulfuron in Flazasulfuron technical (i.e. Technical Grade Active Ingredient or TGAI). This method is also applicable to the determination of Flazasulfuron in the formulation Flazasulfuron 25 WG.

2.2 Outline of method

Flazasulfuron is determined in the test samples by reversed-phase high performance liquid chromatography using ultraviolet detection at 260 nm. Quantification is done by external standardization.

2.3 Procedure

Each sample was analyzed by four independent determinations (n_i = 4). The samples were analyzed in a first run (Day 1) by duplicate injections of two weighings for each sample. The sequence was repeated on a second date (Day 2) with two other weighings of each sample. The Flazasulfuron content for each injection was calculated using the mean response factor from the calibration solutions bracketing the injections of the sample solutions (single point calibration). For the calculation of the content of a sample, the mean value of the duplicate injections was used. For further details, please see attached full method description.

3 REMARKS OF PARTICIPANTS

3.1 Analytical Conditions

Lab	Liquid chromatograph; Detector; Injector	Column	Mobile phase [(1)]	T (°C)	Flow (ml/min)	Vol inj (µl)
1	HP (Agilent) 1090 Series II; DAD II; Automatic	Agilent - HPLC Cartrige 250-4 (LiChrospher 100 RP-18e; 250 mm x 4,6 mm x 5 µm); Serialnumber: 138402	Water (0,05 % acetic acid):Acetonitrile (45:55, v/v)	40	1	10
2	HPLC Varian; Varian 9050; Automatic, Varian ProStar	Luna C18(2) 100A; 150mm x 4.6mm x 5µm; 529946-4	H2O+0.05%Hac / ACN : 45 / 55	40	1	10
3	Waters Alliance 2695 Separation Module; Waters 996 PAD; Automatic	Agilent Zorbax Eclipse XDB C18, 5 µm, 250 x 4.6 mm i.d.; Serial No. US41H00189	water + 0.05 % acetic acid - acetonitrile (45-55 v/v)	40	1	10
4	Elite Lachrom; UV Detector L-2400	Eclipse XDB-C18; 5µm; 4.6 x 250 mm; Agilent, Art. Nr: 990967-902 Serial Nr: USNHOZ7772	Water (0.05% acetic acid)/Acetonitrile (45:55)	40	1	10
5	Agilent HPLC-DAD 1200; Automatic	Aichrombond-AQ C18 4.6mmx250mm, 5micron; serial No. SKH060419	water (0.05% acetic acid):acetonitrile (45:55, v/v)	40	1	10

6	Agilent 1260; DAD; Automatic	Agilent ZORBAX Eclipse XDB-C18, 4,6x250mm, 5µm; Serial-No.: USNH005742	A: 45% demin. Water + 0,05% Acetic acid B: 55% Acetonitrile	40	1	10
7	Agilent 1100; Automatic	Phenomenex Luna C18(2) 100A (250x4.6mm); Serial No. 382218-8	Acetonitrile/0.05% acetic acid in water (55:45)	30	1.2	10
8	Dionex; UVD 170S; Automatic, Dionex ASI 100	Agilent Zorbax SB-C18, 4.6x250mm, 5µm; USCL 020208	0,05% acetic acid:acetonitrile 45:55	25	1	5
9	SHIMADZU 20 AT; UV, SPD 20A; Manual, CTO-10 AS VP	250 x 4.6 mm (i.d), packed with C18, 5 µm, Thermo science ODS HYPERSIL; P/No = 30105-254630, S/No = 0903388M3	Water (0.05% Acetic Acid) : Acetonitril (45:55)	40	1	(10) Not specified
10	AGILENT 1100 SERIES; DAD G1315B; G1313A, automatic	AGILENT ZORBAX ECLIPSE - 250 X 4.6mm 5µm; USNH014600	100% H20(0.05% Acetic Acid) : ACETONITRILE (45:55v/v)	40	1	10
11	Perkin Elmer, Series 200 pump; Flexar PDA; Autosampler	Agilent Zorbax Eclipse XDB C18, 4.6 x 250 mm; 5 µm; Serial No. USNH027938	CH_3CN/H_2O acidified 0.05% acetic acid (55:45, v/v)	40	1	10
12	VARIAN Pro Star, pump 230, column thermostat 550; PDA Detector VARIAN 330; Auto-sampler 430	VARIAN 250mm lenght, 4.6 mm internal diametar, 5µm partical size, Microsorb 100 C18 packing material; Serial No: 279183	Water(0.05% acetic acid):acetonitrile (45:55, v/v)	40	1	10
13	Varian Pro Star; UV-VIS Varian Pro Star Model 345; Automatic	Agilent Zorbax Eclipse XDB-C18, 4.6x250mm, 5-micron; S.N.USNH026707	water (0.05%acetic acid) : acetonitrile (45:55,v/v)	40	1	10
14	Agilent Techn 1200 Series ; Diode Array SL, G1315D; G1367B, automatic	Lichrospher 100 RP-18, 4.6 mm i.d. × 250 mm, 5 µm; serial No.: 029823	water (0.05% acetic acid) : acetonitrile = 45 : 55 (v/v)	40	1	10
15	HPLC Agilent 1100 Series; VWD; Automatic	Zorbax Eclipse XDB-C18, 4.6 x 250mm, 5µm; S.No.: USXW000590	Acetonitrile: 0,05% aqueous acetic acid (55:45)	40	1	10

16	HP 1050; 1090 DAD; HP 1050, automatic	250 x 4.6 mm Zorbax Eclipse XDB-C18, 5 µm (Crawford Scientific); s/n USNH006801	water (0.05% acetic acid):acetonitrile (45:55, v/v)	40	1	10

T = Temperature Vol inj = Volume injected
(1) Isocratic

3.2 Remarks

Several labs made comments about the performance of the method and noted deviations from the method that occurred:

Lab 1 It is a rapid and uncomplicated method. No deviations.

Lab 2 Size of the column: I used a column of 150mm instead of 250mm. PE/100ml ACN => US'15'.
Run time: 7min.

Lab 3 The volumetric flasks were filled up to volume at 20°C ± 1°C instead of at room temperature.

Lab 4 The analysis run well and robuste.

Lab 5 No comments and deviations.

Lab 6 Type of Integrator: DIONEX Chromeleon
Used 0,45µm-filters: Chromafil Xtra, Macherey&Nagel, RC 45/25

Lab 7 The 25 WG samples have not been ground. About 2 mL water have been added previously instead.

Lab 8 No comments.

Lab 9 We used column from Hypersil, different with reference method (Agilent Zorbax XDB), but both of column have a same content. Beside that we used same method and HPLC condition with reference. The column give retention time approx. 5.2 min not really different from reference method who state retention time approx. 6 min.

Lab 10 The analysis went well. For WG samples, c. 4-5g of sample ground in mortar-and-pestle prior to weighing.

Lab 11 No comments and deviations.

Lab 12 The method proposed for the analysis fit the purpose. I have used 20 mg of the standard in the 50 ml flasks. I did validation of the method performance. The linearity in the range from 5 mg till 25 mg was with correlation coefficient of 0,9986. Precision for 5 (separate samples) on the day 1 was with RSD of 0,56%, on the second day was 0.96%. The accuracy of the method was with recoveries 99% to 102% for the both days.

Preparing of the standards and samples was very easy and was not time consuming. Proposed time for sonication of the samples was not sufficient, I used for all 3 samples 3 x 10 min, and shaking between.
I have earlier ret time and it was approximately at 5.28 min.
General the test method is very nice and user friendly.
The chromatography system that we have it's relatively new, but we do not have UPS that will make constant current during performing the analysis.

Lab 13 No comments and deviations.

Lab 14 No comments.

Lab 15 For preparation of calibration/sample solution we used 25 ml volumetric flasks, maintaining the prescribed final concentration.

Lab 16 No comments and deviations.

4 RESULTS AND DISCUSSION

The statistical evaluation of the collaborative trial was performed according to DIN ISO 5725. Samples were sent to 16 laboratories. All laboratories sent back results and the results reported by the participants were all used. Lab 5 only determined the content of Flazasulfuron in formulation samples and consequently was included only for evaluation of those data. The assay results reported by the laboratories are listed in Tables 2-6, and are presented in Figures 1-5.

Statistical evaluation of the data was done following "Guidelines for CIPAC Collaborative Study Procedures for Assessment of Performance of Analytical Methods." The data were examined for outliers and stragglers using Cochran's test on the within-lab variability, followed by Grubbs-I test on the laboratory means, and iterating where necessary. Where deemed necessary, an additional Grubbs-II test was conducted to identify two stragglers or outliers. The tests were performed at an alpha level of 0.01 for outlier, and 0.05 for straggler. Based on this procedure, the Cochran and Grubb tests identified the following potential outlier and straggler lab data from the sample sets. Straggler and outlier values are reported below.

Flazasulfuron determination				
Code Sample	**Cochran Straggler**	**Cochran Outlier**	**Grubbs-I Straggler**	**Grubbs-I Outlier**
Tech-1	none	Lab 9, 11, 12	none	Lab 11
Tech-2	Lab 9, 12	Lab 2, 11	none	Lab 11
Flazasulfuron 25 WG - 1	none	Lab 11, 12	none *	none
Flazasulfuron 25 WG - 2	Lab 9	Lab 11	none	Lab 11
Flazasulfuron 25 WG - 3	Lab 9	Lab 11	none	Lab 11

* Lab 11 and 12 were identified as straggler pair by Grubbs-II

A summary of the statistical evaluation for the labs is given in Table 1, which includes the repeatability and reproducibility values, as well as the between-lab experimental Reproducibility Relative Standard Deviation, $\%RSD_R$ and the calculated acceptable value, $\%RSD_{R(Hor)}$, based on the Horwitz curve calculation.

4.1 Flazasulfuron

Tech-1

Three outliers were detected by the Cochran test of variance homogeneity. Variance from Lab 11 is the highest and the mean value at 1024.2 g/kg was significantly higher than the others, which was detected also by the Grubbs-I test between all labs. The lab 11 value is maintained in the statistical evaluation presented in Table 1A, but was removed for evaluation in the refined Table 1B. This refinement did have a small impact on the observed overall mean value, and did improve significantly the Repeatability and Reproducibility parameters.

The statistical analysis of these results show the Repeatability Relative Standard Deviation ($\%RSD_r$) and the between-lab Reproducibility Relative Standard Deviation ($\%RSD_R$) for the determination of Flazasulfuron in Flazasulfuron technical 1 sample to be well below the limit calculated ($\%RSD_{R(Hor)}$) using the Horwitz equation, even before excluding lab 11.

Tech-2

Two stragglers and two outliers were detected by the Cochran test of variance homogeneity. Variance from Lab 11 is the highest and the mean value at 1021.9 g/kg was significantly higher than the others, which was detected also by the Grubbs-I test between all labs. The lab 11 value is maintained in the statistical evaluation presented in Table 1A, but was removed for evaluation in the refined Table 1B. This refinement did have a small impact on the observed overall mean value, and did improve significantly the Repeatability and Reproducibility parameters.

The statistical analysis of these results show the Repeatability Relative Standard Deviation ($\%RSD_r$) and the between-lab Reproducibility Relative Standard Deviation ($\%RSD_R$) for the determination of Flazasulfuron in Flazasulfuron technical 2 sample to be well below the limit calculated ($\%RSD_{R(Hor)}$) using the Horwitz equation, even before excluding lab 11.

Flazasulfuron 25 WG-1

Two outliers were detected by the Cochran test of variance homogeneity for Lab 11 and Lab 12. Variance for both labs is significantly higher, and they were identified as straggler pair by the Grubbs-II test for all labs. The lab 11 and Lab 12 values are maintained in the statistical evaluation presented in Table 1A, but were removed for evaluation in the refined Table 1B. This refinement did have a small impact on the observed overall mean value, and did improve the Repeatability and Reproducibility parameters.

The statistical analysis of these results show the Repeatability Relative Standard Deviation ($\%RSD_r$) and the between-lab Reproducibility Relative Standard Deviation ($\%RSD_R$) for the determination of Flazasulfuron in Flazasulfuron 25 WG-1 sample to be well below the limit calculated ($\%RSD_{R(Hor)}$) using the Horwitz equation, even before excluding Labs 11 and 12.

Flazasulfuron 25 WG-2

An outlier was detected by the Cochran test of variance homogeneity for Lab 11. Variance from Lab 11 is the highest and the mean value at 271.8 g/kg was significantly higher than the others, which was detected also by the Grubbs-I test for all labs. A further Cochran straggler was found for Lab 9, which was maintained. The lab 11 value is maintained in the statistical evaluation presented in Table 1A, but was removed for evaluation in the refined Table 1B. This refinement did have a small impact on the observed overall mean value, and did improve the Reproducibility parameter especially.

The statistical analysis of these results show the Repeatability Relative Standard Deviation ($\%RSD_r$) and the between-lab Reproducibility Relative Standard Deviation ($\%RSD_R$) for the determination of Flazasulfuron in Flazasulfuron 25 WG-2 sample to be below the limit calculated ($\%RSD_{R(Hor)}$) using the Horwitz equation, even before excluding Lab 11.

Flazasulfuron 25 WG-3

One outlier was detected by the Cochran test of variance homogeneity for Lab 11. Variance from Lab 11 is the highest and the mean value at 270.8 g/kg was significantly higher than the others, which was detected also by the Grubbs-I test for all labs. A further Cochran straggler was found for Lab 9, which was maintained. The lab 11 value is maintained in the statistical evaluation presented in Table 1A, but was removed for evaluation in the refined Table 1B. This refinement did have a small impact on the observed overall mean value, and did improve the Reproducibility parameter especially.

The statistical analysis of these results show the Repeatability Relative Standard Deviation ($\%RSD_r$) and the between-lab Reproducibility Relative Standard Deviation ($\%RSD_R$) for the determination of Flazasulfuron in Flazasulfuron 25 WG-3 sample to be below the limit calculated ($\%RSD_{R(Hor)}$) using the Horwitz equation, even before excluding Lab 11.

5 CONCLUSION

After examination of all provided laboratory data and identification of stragglers and outliers, retention of all laboratory data was statistically valid for the determination of Flazasulfuron in Flazasulfuron technical. Lab 11 showed high within-lab variability and consistently higher results, identified by both Cochran and Grubbs as outlier. Although it was not strictly necessary, a refined statistical analysis without this lab was done.

After examination of all provided laboratory data and identification of stragglers and outliers, retention of all laboratory data was statistically valid for the determination of Flazasulfuron in Flazasulfuron formulation. Nevertheless, a refinement was proposed after removal of lab 11 (identified by both Cochran and Grubbs as outlier) for the three formulation samples. Lab 12 was also removed for the WG-1 sample. Removal of the outliers improved the statistical evaluation, especially for the Reproducibility parameter.

The between-lab Reproducibility Relative Standard Deviation ($\%RSD_R$) and the Repeatability Relative Standard Deviation ($\%RSD_r$) were well below the limit calculated ($\%RSD_{R(Hor)}$) using the Horwitz equation for the determination of Flazasulfuron in Flazasulfuron technical and Flazasulfuron formulation with no outlier removed. After removal of the outliers, $\%RSD_R$ and $\%RSD_r$ improved further.

The acceptance of this method as an approved CIPAC assay method for Flazasulfuron in Flazasulfuron technical and Flazasulfuron formulation is recommended.

ACKNOWLEDGEMENTS

ISK wishes to thank all the laboratories and their staff who participated in this study.

TABLES (1-6)

TABLE 1A - Flazasulfuron – Summary of the statistical evaluation of the collaborative Study Data
All Test Results Retained (No outlier removed)

			Flazasulfuron 25 WG		
	Tech-1	**Tech-2**	**WG-1**	**WG-2**	**WG-3**
No. of Labs	15	15	16	16	16
No. of Stragglers	0	$2^{(c)}$	$2^{(g)}$	$1^{(c)}$	$1^{(c)}$
No. of Outliers	$3^{(C,G)}$	$2^{(C,G)}$	$2^{(C)}$	$1^{(C,G)}$	$1^{(C,G)}$
No. of Labs Retained	15	15	16	16	16
No. of Results	60	60	64	64	64
Total Mean, **X** (g/kg)	985.1	981.8	257.4	258.6	257.2
Repeatability standard deviation $\mathbf{S_r}$	11.1	14.0	2.80	2.50	2.85
"Pure" between laboratory standard variation $\mathbf{S_L}$	11.4	10.4	4.39	4.43	4.44
Reproducibility standard deviation $\mathbf{S_R}$	15.9	17.4	5.20	5.09	5.28
Repeatability **r**	31.1	39.1	7.84	7.01	7.99
Reproducibility within lab $\mathbf{R_L}$	32.0	29.2	12.3	12.4	12.4
Reproducibility between labs **R**	44.6	48.8	14.6	14.2	14.8
RSD_r (%)	1.13	1.42	1.09	0.97	1.11
RSD_R (%)	1.62	1.78	2.02	1.97	2.05
$RSD_{R(Hor)}$ (%)	2.01	2.01	2.45	2.45	2.45

Limits (g/kg)

X+R	1029.7	1030.6	272.0	272.8	272.0
X+r	1016.2	1020.9	265.3	265.6	265.2
X-r	954.0	942.8	249.6	251.6	249.2
X-R	940.5	933.0	242.8	244.3	242.4

$^{(C,c)}$ from Cochran test
$^{(G,g)}$ from Grubbs-I test

Where :

X	= average
S_r	= repeatability standard deviation
S_L	= "pure" between laboratory standard deviation
S_R	= reproducibility standard deviation = $(S_r^2 + S_L^2)^{0.5}$
r	= repeatability within-lab (2.8 S_r)
R	= reproducibility between labs (2.8 S_R)
R_L	= reproducibility within lab on different days (2.8 S_L)
% RSD_r	= repeatability relative standard deviation (100 S_r/X)
% RSD_R	=reproducibility relative standard deviation between labs (100 S_R/X)
% $RSD_{R(Hor)}$	= Horowitz value calculated from $2^{(1-0.5\log c)}$ where c is the concentration of the analyte as a decimal fraction (e.g. for 100% concentration c = 1)

TABLE 1B - Flazasulfuron – Summary of the statistical evaluation of the collaborative Study Data Selected Outlier Test Results Removed

			Flazasulfuron 25 WG		
	Tech-1	**Tech-2**	**WG-1**	**WG-2**	**WG-3**
No. of Labs	15	15	16	16	16
No. of Stragglers	0	2[(c)]	0	1[(c)]	1[(c)]
No. of Outliers	2[(C)]	1[(C)]	0	0	0
No. of Labs Retained	14	14	14	15	15
No. of Results	56	56	56	60	60
Total Mean, **X** (g/kg)	982.3	979.0	256.1	257.7	256.3
Repeatability standard deviation $\mathbf{S_r}$	7.33	6.06	1.50	1.89	2.31
"Pure" between laboratory standard variation $\mathbf{S_L}$	5.75	5.40	2.63	2.80	2.72
Reproducibility standard deviation $\mathbf{S_R}$	9.32	8.12	3.03	3.38	3.57
Repeatability **r**	20.5	17.0	4.20	5.30	6.47
Reproducibility within lab $\mathbf{R_L}$	16.1	15.1	7.38	7.84	7.61
Reproducibility between labs **R**	26.1	22.7	8.49	9.47	9.99
RSD_r (%)	0.75	0.62	0.56	0.74	0.90
RSD_R (%)	0.95	0.83	1.18	1.31	1.39
$RSD_{R(Hor)}$ (%)	2.01	2.01	2.46	2.45	2.46

Limits (g/kg)

X+R	1008.4	1001.7	264.6	267.1	266.3
X+r	1002.9	995.9	260.3	263.0	262.8
X-r	961.8	962.0	251.9	252.4	249.8
X-R	956.2	956.2	247.6	248.2	246.3

[(C,c)] from Cochran test
[(G,g)] from Grubbs-I test

Where :

X	= average
S_r	= repeatability standard deviation
S_L	= "pure" between laboratory standard deviation
S_R	= reproducibility standard deviation = $(S_r^2 + S_L^2)^{0.5}$
r	= repeatability within-lab (2.8 S_r)
R	= reproducibility between labs (2.8 S_R)
R_L	= reproducibility within lab on different days (2.8 S_L)
% RSD_r	= repeatability relative standard deviation (100 S_r/X)
% RSD_R	=reproducibility relative standard deviation between labs (100 S_R/X)
% $RSD_{R(Hor)}$	= Horowitz value calculated from $2^{(1-0.5\log c)}$ where c is the concentration of the analyte as a decimal fraction (e.g. for 100% concentration c = 1)

TABLE 2 - Assay Results Summary by Lab for Flazasulfuron in Flazasulfuron Technical, Tech-1
All values in [g/kg]

	DAY 1		DAY 2				
LAB	A	B	A	B	Mean	SD	Notes
1	977.42	973.27	969.83	976.60	974.28	3.47	
2	989.41	989.87	1001.55	998.65	994.87	6.16	
3	983.02	976.70	988.39	974.44	980.64	6.32	
4	982.16	980.77	990.07	990.23	985.81	5.05	
6	986.07	986.43	988.27	987.60	987.09	1.02	
7	991.15	990.69	992.25	990.52	991.16	0.78	
8	989.02	988.18	987.37	988.41	988.25	0.68	
9	1000.40	970.85	990.11	989.63	987.75	12.31	C
10	971.29	974.84	970.61	978.90	973.91	3.81	
11	1009.99	985.39	1052.38	1049.12	1024.22	32.26	C, G
12	990.46	991.33	947.92	963.77	973.37	21.25	C
13	967.52	972.64	980.71	974.53	973.85	5.45	
14	979.36	979.76	978.49	978.20	978.95	0.73	
15	976.96	977.14	987.74	973.29	978.78	6.23	
16	985.55	983.92	983.46	982.29	983.81	1.35	

SD = Standard deviation

c-Cochran straggler, **C**-Cochran outlier, **g**-Grubb straggler, **G**-Grubb outlier

TABLE 3 - Assay Results Summary by Lab for Flazasulfuron in Flazasulfuron Technical, Tech-2
All values in [g/kg]

	DAY 1		DAY 2				
LAB	A	B	A	B	Mean	SD	Notes
1	975.36	975.11	984.83	975.44	977.69	4.765	
2	980.92	984.31	1004.25	994.37	990.96	10.540	C
3	976.98	966.09	976.26	980.58	974.98	6.216	
4	975.83	977.69	979.16	979.55	978.06	1.688	
6	983.45	978.73	980.94	980.77	980.97	1.932	
7	992.37	990.42	990.19	990.67	990.91	0.992	
8	985.30	985.01	986.39	983.64	985.09	1.132	
9	984.54	961.92	994.12	982.48	980.77	13.549	c
10	971.41	970.83	972.81	981.06	974.03	4.760	
11	992.30	969.24	1056.91	1069.15	1021.90	48.671	C, G
12	987.89	967.63	963.30	967.75	971.64	11.026	c
13	972.18	969.54	975.71	970.05	971.87	2.806	
14	979.58	974.86	973.32	971.81	974.90	3.364	
15	968.65	969.23	977.77	975.39	972.76	4.522	
16	980.21	979.83	982.57	981.28	980.97	1.231	

SD = Standard deviation

c-Cochran straggler, **C**-Cochran outlier, **g**-Grubb straggler, **G**-Grubb outlier

TABLE 4 - Assay Results Summary by Lab for Flazasulfuron in Water Dispersible Granules (25 WG) Flazasulfuron 25 WG-1; All values in [g/kg]

	DAY 1		DAY 2				
LAB	A	B	A	B	Mean	SD	Notes
1	257.17	254.86	259.38	257.90	257.33	1.89	
2	256.76	256.13	258.05	260.92	257.97	2.13	
3	250.91	250.17	253.57	252.59	251.81	1.55	
4	257.83	257.98	259.17	258.69	258.42	0.63	
5	253.06	252.97	254.49	254.26	253.69	0.79	
6	259.76	260.30	258.60	259.18	259.46	0.74	
7	257.28	255.95	253.00	253.29	254.88	2.08	
8	261.53	261.08	261.06	262.37	261.51	0.61	
9	260.07	258.28	256.33	255.23	257.48	2.14	
10	254.39	255.52	253.86	249.40	253.29	2.69	
11	262.35	264.91	275.31	274.15	269.18	6.51	C, g
12	260.21	263.75	273.93	258.71	264.15	6.85	C, g
13	253.67	253.78	250.21	249.85	251.88	2.14	
14	258.28	258.69	258.77	256.69	258.11	0.97	
15	255.40	255.63	253.20	254.73	254.74	1.10	
16	255.27	255.26	253.57	254.97	254.77	0.81	

SD = Standard deviation

c-Cochran straggler, **C**-Cochran outlier, **g**-Grubb straggler, **G**-Grubb outlier

TABLE 5 - Assay Results Summary by Lab for Flazasulfuron in Water Dispersible Granules (25 WG) Flazasulfuron 25 WG-2; All values in [g/kg]

	DAY 1		DAY 2				
LAB	A	B	A	B	Mean	SD	Notes
1	258.22	258.75	259.89	260.18	259.26	0.93	
2	255.20	256.32	261.80	260.18	258.37	3.12	
3	250.34	252.54	248.55	252.61	251.01	1.95	
4	259.98	259.55	260.32	261.53	260.34	0.85	
5	255.19	255.36	254.77	256.09	255.35	0.55	
6	262.51	262.17	258.81	259.40	260.72	1.89	
7	257.00	257.25	257.67	254.34	256.57	1.51	
8	260.90	260.86	260.78	261.47	261.00	0.32	
9	262.94	261.10	254.15	255.59	258.44	4.23	
10	256.10	256.39	253.28	255.83	255.40	1.43	
11	265.84	267.05	279.63	274.82	271.84	6.54	C, G
12	263.07	263.15	258.42	257.31	260.49	3.06	
13	253.26	253.48	250.44	251.52	252.17	1.45	
14	259.58	259.23	258.74	257.35	258.72	0.98	
15	260.00	259.94	258.12	261.16	259.80	1.25	
16	257.95	257.86	255.37	258.53	257.43	1.40	

SD = Standard deviation

c-Cochran straggler, **C**-Cochran outlier, **g**-Grubb straggler, **G**-Grubb outlier

TABLE 6 - Assay Results Summary by Lab for Flazasulfuron in Water Dispersible Granules (25 WG) Flazasulfuron 25 WG-3; All values in [g/kg]

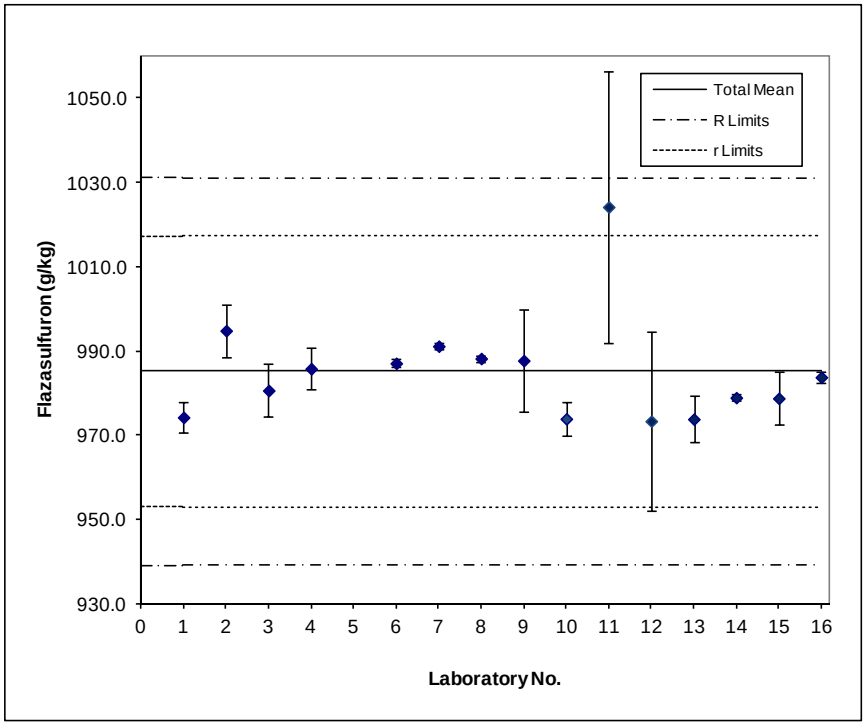
	DAY 1		DAY 2				
LAB	A	B	A	B	Mean	SD	Notes
1	259.30	259.66	256.38	256.90	258.06	1.66	
2	253.61	252.86	259.33	259.34	256.28	3.54	
3	255.23	254.82	254.83	255.38	255.07	0.28	
4	259.05	256.84	258.90	259.68	258.62	1.23	
5	254.74	253.64	255.42	256.20	255.00	1.09	
6	261.61	260.17	258.72	258.38	259.72	1.48	
7	254.79	253.16	256.56	257.39	255.47	1.89	
8	261.49	261.40	261.74	261.72	261.59	0.17	
9	249.31	249.61	258.76	257.58	253.82	5.05	c
10	256.05	256.14	253.37	248.43	253.50	3.61	
11	265.78	264.39	275.56	277.54	270.82	6.69	C, G
12	262.61	261.54	256.54	255.34	259.01	3.60	
13	249.92	250.58	249.67	248.76	249.73	0.75	
14	259.58	259.31	257.29	257.13	258.32	1.30	
15	257.13	258.26	256.72	255.72	256.96	1.05	
16	256.25	253.92	250.14	252.36	253.17	2.58	

SD = Standard deviation

c-Cochran straggler, **C**-Cochran outlier, **g**-Grubb straggler, **G**-Grubb outlier

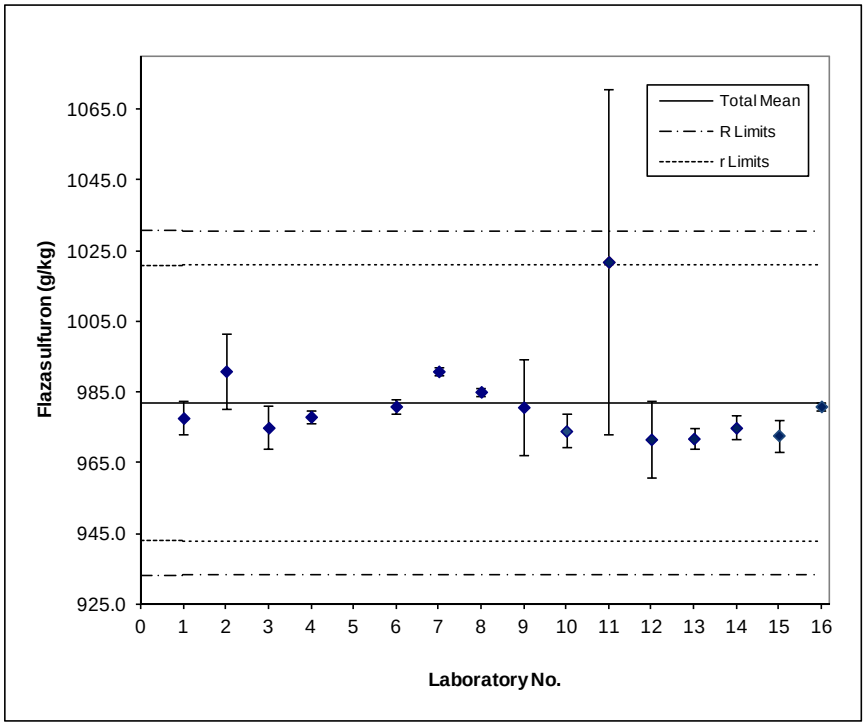
FIGURES (1-5)

FIGURE 1 - Flazasulfuron in Flazasulfuron Technical, Tech-1



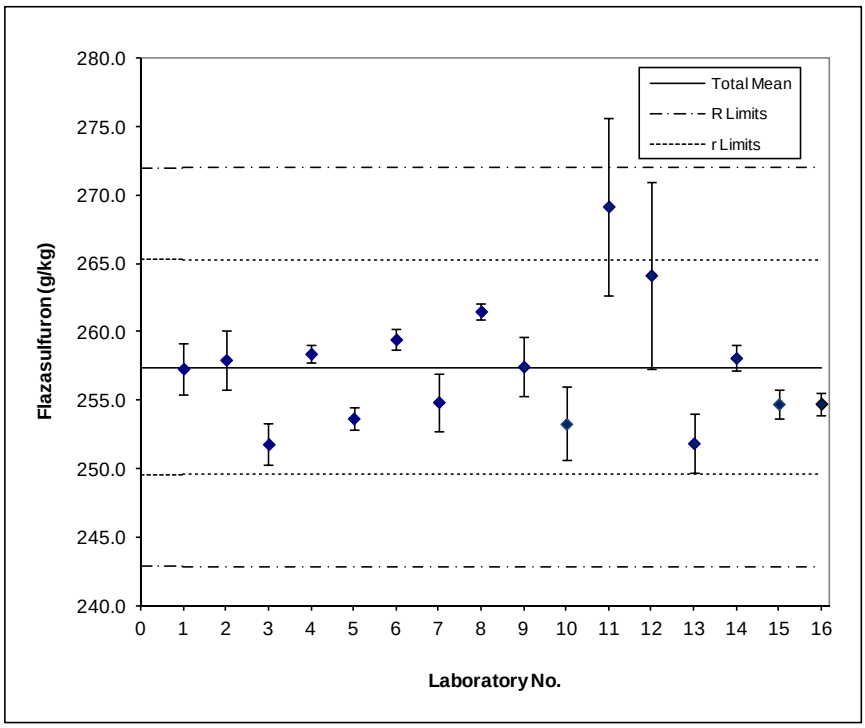
ni = 4 for all Labs

FIGURE 2 - Flazasulfuron in Flazasulfuron Technical, Tech-2



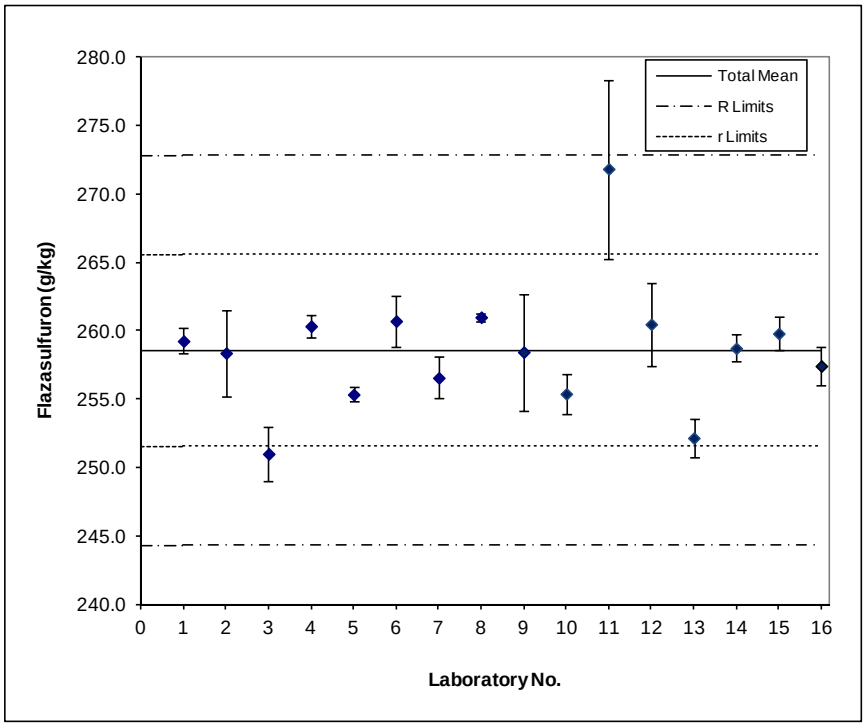
ni = 4 for all Labs

FIGURE 3 - Flazasulfuron in Water Dispersible Granules (25WG), Flazasulfuron 25 WG-1



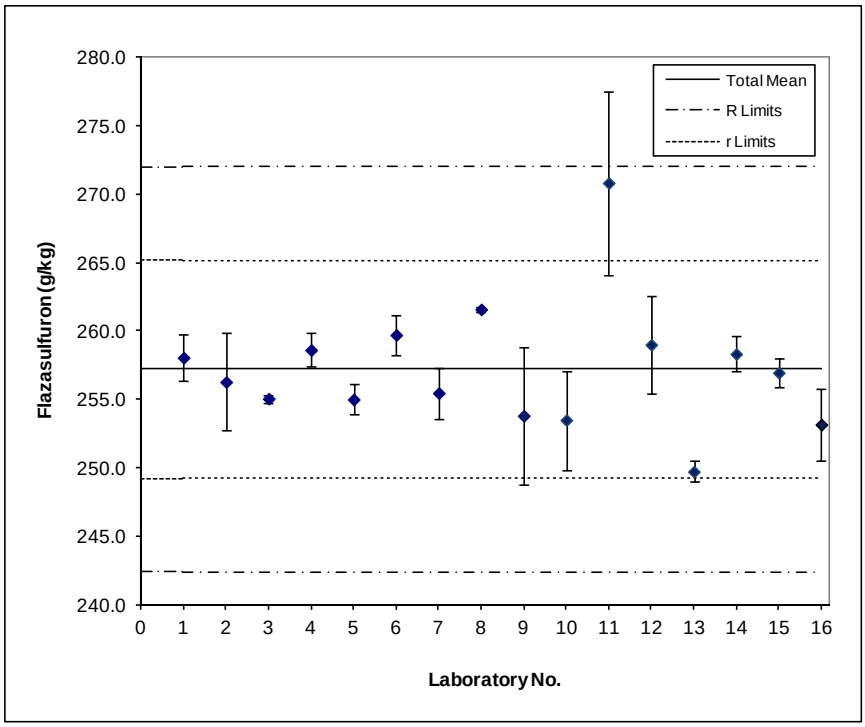
ni = 4 for all Labs

FIGURE 4 – Flazasulfuron in Water Dispersible Granules (25WG), Flazasulfuron 25 WG-2



ni = 4 for all Labs

FIGURE 5 - Flazasulfuron in Water Dispersible Granules (25WG), Flazasulfuron 25 WG-3



ni = 4 for all Labs