1. INTRODUCTION

Background and Objective:

Initially, the objective of this study was to adapt/develop and to validate an analytical method for the determination of pendimethalin (BAS 455 H) and two metabolites, M455H001 (Reg. No. 4108474) and Reg. No. 4061757, in soil with a target limit of quantitation (LOQ) of 0.010 mg/kg (10 µg/kg) for each analyte. At the Sponsor's request, this method was adapted/developed and validated to include a third pendimethalin metabolite, Reg. No. 4982164 (P36), in soil and sediment also with a target limit of quantitation (LOQ) of 0.010 mg/kg (10 µg/kg). This metabolite occurred only in the sediment of an aquatic metabolism study.

2. EXPERIMENTAL

2.1 Test System

Two soil types, used in related soil degradation studies (Li 10 and Bruch West), and one sediment sample.

The two soils have been characterized as follows:

Soil Identification	BASF Soil Sample No.	Soil Type (USDA)	Organic Carbon (TOC, %)	pH[2]	Clay[3] (%)	Water Content (g H_2O/100 g TS)
Bruch West	12/060/02	sandy loam	1.36	7.4	11.0	7
Li10	12/1680/02	loamy sand	0.97	6.2	4.6	6

The sediment has been characterized as follows:

Sediment Identification	BASF Soil Sample No.	Soil Type (USDA)	Organic Carbon (TOC, %)	pH[2]	Clay[3] (%)	Water Content (g H_2O/100 g TS)
Ranschgraben	11/1723/01	loamy sand	3.27	6.5	8.6	48

Soil and sediment samples were stored at room temperature in the dark when not in use.

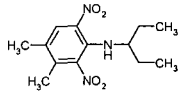
2.2 Analytical Test and Reference Items

The following standards, provided by the Sponsor (Appendix 1), were used as test and reference items:

[2] $CaCl_2$.

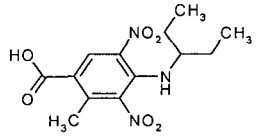
[3] particle size distribution <0.002 mm.

Pendimethalin (BAS 455 H) (Reg. No. 900072)



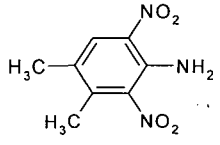
IUPAC Name: N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine
Empirical formula: $C_{13}H_{19}N_3O_4$ Molar mass: 281.3 g/mol
CAS No.: 40487-42-1 Purity: 99.2%

Pendimethalin Metabolite M455H001 (Reg. No. 4108474)



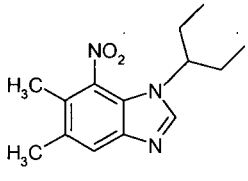
IUPAC Name: 4-[(1-ethylpropyl)amino]-2-methyl-3,5-ditrobenzoic acid
Empirical formula: $C_{13}H_{17}N_3O_6$ Molar mass: 311.3 g/mol
CAS No.: none Purity: 99.6%

Pendimethalin Metabolite Reg. No. 4061757



IUPAC Name: 2,6-dintro-3,4-dimethylaniline
Empirical formula: $C_8H_9N_3O_4$ Molar mass: 211.2 g/mol
CAS No.: 40318-31-8 Purity: 96.1%

Pendimethalin Metabolite Reg. No. 4982164 (P36)



IUPAC Name: 1-(1-ethylpropyl)-5,6-dimethyl-7-nitro-1H-benzimidazole
Empirical formula: $C_{14}H_{19}N_3O_2$ Molar mass: 261.3 g/mol
CAS No.: none Purity: 99.0%

2.3 Analytical Method

2.3.1 Apparatus

2.3.1.1 Laboratory Equipment

XP205DR analytical balance, Mettler-Toledo.

ED 2202S-CW balance, Sartorius.

HS250B and HS260B horizontal shaker, IKA Labortechnik.

Transsonic 460 bath, Elma Hans Schmidbauer.

Rotixa 50S centrifuge, Hettich.

Vortex mixer REAX top, Heidolph.

Typical glassware and laboratory equipment.

All glassware was cleaned in a laboratory dishwasher and air-dried before use.

2.3.1.2 LC/MS/MS System

Pendimethalin and Reg. No. 4982164 (P36) were quantified with positive ion LC/MS/MS and metabolite M455H001 with negative ion LC/MS/MS using:

Applied Biosystems API 4000 LC/MS system (vacuum solvent degasser, binary LC pump, column oven) and CTC Analytics HTC-Pal autosampler. AB Sciex API 4000 triple quadrupole LC/MS/MS system with TurboIonspray source. Analyst 1.4.2 instrument control and data acquisition software.

2.3.1.3 GC/MS/MS System

Pendimethalin metabolite Reg. No. 4061757 was quantified using:
Thermo TSQ Quantum GC/MS System equipped with TriPlus AS autosampler, Trace Ultra GC gas chromatograph, temperature programmable PTV and split/splitless injector, digital pressure and flow control DPFC.

2.3.2 Solvents and Chemicals

Formic acid (98%-100%) (Sigma Aldrich)

Hydrochloric acid (32 % = 10 M) (Merck)

Millipore Water (PTRL Europe)

Acetone, for pesticide residue analysis, Promochem

Acetonitrile, HPLC Grade, Promochem

Methanol, HPLC Grade, Promochem

2.3.3 Preparation of Standard Solutions

Stock solutions of pendimethalin and its three metabolites were prepared in acetone, as shown in the following table:

Substance Name	Weight [mg]	Dissolve in [mL]	Obtain [mg/mL] (*)
Pendimethalin (BAS 455 H) (purity: 99.2 %)	10.77	10.684	1.0
Pendimethalin Metabolite M455H001 (purity: 99.6%)	11.30	11.255	1.0
Pendimethalin Metabolite Reg. No. 4061757 (purity: 96.1%)	10.67	10.254	1.0
Pendimethalin Metabolite Reg. No. 4982164 (purity: 99.0%)	10.17	10.069	1.0

(*): corrected for purity

Separate fortification solutions for pendimethalin and its three metabolites, with concentrations of 10 µg/mL and 1.0 µg/mL, were prepared in acetone by accurate dilution of the stock solutions.

Calibration solutions containing both pendimethalin and M455H001 and calibration solutions containing Reg. No. 4982164 were prepared by volumetric dilution with acetonitrile/water [50/50 (v/v)] + 0.1% formic acid to obtain concentrations of 10 µg/mL and 0.10µg/mL (intermediate solutions), and 0.025, 0.10, 0.50, 1.0, 2.5 and 5.0 ng/mL.

Calibration solutions containing the metabolite Reg. No. 4061757 were prepared by volumetric dilution with acetone to obtain concentrations of 10 µg/mL (intermediate solution), and 1.0, 2.5, 5.0, 10, 25, 50 and 100 ng/mL.

In order to demonstrate matrix effects for pendimethalin and M455H001 in soil and Reg. No. 4982164 (P36) in sediment and soil, calibration solutions were added to extracts from blank controls to obtain concentrations of 1.0 ng/mL and 0.1 ng/mL (solvent/matrix ratio corresponding to a dilution factor of 10 (DF = 10) used for the analysis of samples).

In order to demonstrate matrix effects for the metabolite Reg. No. 4061757, calibration solutions were added to extracts from blank controls to obtain concentrations of 50 ng/mL and 5 ng/mL.

All standard solutions were stored refrigerated in amber glass bottles when not in use.

2.3.4 Stability of Sample Extracts

Stability in the extracts of the two soil types was demonstrated by re-injecting selected samples after at least 4 days of either refrigerator or freezer storage as shown in Table 7 for pendimethalin and metabolite M455H001. The stability for metabolite Reg. No. 4961757 is given in Table 8. For Reg. No. 4982164 (P36) stability in the extracts of one soil and one sediment is given in Table 7, too.

After refrigerated or frozen storage, the recoveries for all four analytes in the extracts of both soil types and one soil sediment were all still within the acceptable range of 70% to 110%, thus stability under refrigerated or frozen conditions was considered sufficiently proven.

2.3.5 Sample Analysis

2.3.5.1 Sample Preparation and Fortification:

Weigh 10.0 g of soil or sediment sample into 50 mL PE centrifuge tube.

For fortifications, add 100 µL of the appropriate spike solution (1.0 µg/mL or 10 µg/mL, for example) to the untreated soil or sediment sample.

2.3.5.2 Sample Extraction for Pendimethalin, M455H001 and Reg. No. 4982164 (P36):

- Add 20 mL of 2% HCl in methanol and shake for 30 minutes on a mechanical shaker at 225 rpm and sonicate for 10 minutes.
- Separate soil from the extraction solvent by centrifugation at 4000 rpm for 5 minutes.
- Decant the supernatant into a 100 mL graduated cylinder.
- Add 20 mL of methanol/water [7:3 (v/v)] and shake for 30 minutes on a mechanical shaker at 225 rpm and sonicate for 10 minutes.
- Separate soil from extraction solvent by centrifugation at 4000 rpm for 5 minutes.
- Decant the supernatant and combine with previous soil extract.
- Add 20 mL of methanol/water [1:1 (v/v)] and shake for 30 minutes on a mechanical shaker at 225 rpm and sonicate for 10 minutes.
- Separate soil from the extraction solvent by centrifugation at 4000 rpm for 5 minutes.
- Decant the supernatant and combine with previous soil extracts.
- Bring the combined soil extract to a constant volume (60 mL, for sediment fill up to 65 mL) using methanol/water [7:3 (v/v)].
- Prior to LC/MS/MS quantitation, dilute (typically DF = 10) the soil extract with acetonitrile/water [50/50 (v/v)] + 0.1% formic acid.
- Quantify, without further clean-up, using the LC/MS/MS conditions described in Section 2.4.1.

2.3.5.3 Sample Extraction for Reg. No. 4061757:

- Add 10 mL of acetone and shake for 30 minutes on a mechanical shaker at 225 rpm.
- After shaking, sonicate for 10 minutes.
- Separate soil from the extraction solvent by centrifugation at 4000 rpm for 5 minutes.
- Decant the supernatant into a 100 mL graduated cylinder.
- Repeat the first four steps, combining soil extracts.
- Bring the combined soil extract to a constant volume (20 mL) with acetone.
- Quantify, without further clean-up, using the GC/MS/MS conditions described in Section 2.4.2.

2.4 Analysis

2.4.1 LC/MS/MS Analysis

Pendimethalin (BAS 455 H), metabolite M455H001 (Reg. No. 4108474) and metabolite Reg. No. 4982164 (P36) were quantified using the following LC/MS/MS system described below:

LC System	Agilent 1200 SL LC system (vacuum solvent degasser, binary LC pump, column oven), and CTC Analytics HTC-Pal Autosampler			
LC Column	Thermo Betasil C18 column (length: 100 mm, i.d.: 2.1 mm, particle size: 5 µm, oven temp.: 35°C.			
LC Injection Volume	50 µL			
LC Method	Solvent A: Water containing 0.1% formic acid Solvent B: Methanol containing 0.1% formic acid Program:			
	Time (min)	Flow rate (mL/min)	% A	% B
	0.00	0.60	66	34
	2.00	0.60	26	74
	4.00	0.60	10	90
	6.50	0.60	10	90
	6.60	0.60	0	100
	10.00	0.60	0	100
	10.10	0.60	66	34
	12.00	0.60	66	34
Retention times	≈ 5.4 minutes for pendimethalin (BAS 455 H); ≈ 5.0 minutes for metabolite M455H001 (Reg. No. 4108474) and ≈ 4.5 minutes for metabolite P36 (Reg. No. 4982164).			
MS/MS System	Applied Biosystems MDS Sciex API 4000 triple quadrupole LC/MS/MS system with Turbolonspray (ESI) source.			
Ion Source Conditions ESI Positive Polarity				
Pendimethalin and Reg. No. 4982164 (P36)	Source temperature:	450°C		
	Gas supply (GS 1):	40 (arbitrary units)		
	Gas supply (GS 2).	70 (arbitrary units)		
	Curtain gas:	25 (arbitrary units)		
	CAD gas:	5 (arbitrary units)		
	Entrance potential:	10 V		
	IonSpray voltage:	5200 V		
	Resolution:	Q1: Unit, Q3: Unit		
MS/MS Conditions				
Pendimethalin	MS/MS transition for quantification:	282 *m/z* > 194 *m/z* (quantification)		
	Collision energy (CE):	25 V		
	Cell exit potential (CXP):	12 V		
	Dwell time:	200 ms		
	Declustering potential (DP):	36 V		
	MS/MS transition for confirmation:	282 *m/z* > 212 *m/z* (confirmation)		
	Collision energy (CE):	15 V		
	Cell exit potential (CXP):	14 V		
	Dwell time:	200 ms		
	Declustering potential (DP):	36 V		

Reg. No. 4982164 (P36)	MS/MS transition for quantification:	262 *m/z* > 146 *m/z* (quantification)
	Collision energy (CE):	35 V
	Cell exit potential (CXP):	12 V
	Dwell time:	200 ms
	Declustering potential (DP):	46 V
	MS/MS transition for confirmation:	262 *m/z* > 119 *m/z* (confirmation)
	Collision energy (CE):	35 V
	Cell exit potential (CXP):	10 V
	Dwell time:	200 ms
	Declustering potential (DP):	46 V
Ion Source Conditions ESI Negative Polarity		
M455H001	Source temperature:	450°C
	Gas supply (GS 1):	40 (arbitrary units)
	Gas supply (GS 2).	70 (arbitrary units)
	Curtain gas:	25 (arbitrary units)
	CAD gas:	5 (arbitrary units)
	Entrance potential:	-10 V
	IonSpray voltage:	-4500 V
	Resolution:	Q1: Unit, Q3: Unit
MS/MS Conditions		
M455H001	MS/MS transition for quantification:	310 *m/z* > 266 *m/z* (quantification)
	Collision energy (CE):	-14 V
	Cell exit potential (CXP):	-7 V
	Dwell time:	200 ms
	Declustering potential (DP):	-50 V
	MS/MS transition for confirmation:	310 *m/z* > 236 *m/z* (confirmation)
	Collision energy (CE):	-20 V
	Cell exit potential (CXP):	-13 V
	Dwell time:	200 ms
	Declustering potential (DP):	-50 V

Figure 41 to Figure 43 present the full scan product ion spectra of pendimethalin, M455H001 and Reg. No. 4982164 (P36) showing the selection of the two structurally significant product ions used for the LC/MS/MS quantification/confirmation and the parent ion.

For both pendimethalin and M455H001, quantitative determination was carried out by external standardization using calibration standards in solvent. This calibration was preferred compared to matrix based calibration because it is independent from availability of appropriate blank matrix.

Calibration functions ranging from 0.025 ng/mL to 5.0 ng/mL (≥5 levels: 0.025, 0.10, 0.50, 1.0, 2.50 and 5.0 ng/mL) were used to quantify pendimethalin and M455H001 recoveries (Figure 1 through Figure 4). For evaluation of the stability in extracts a calibration function ranging from 0.10 ng/mL to 5.0 ng/mL with 3 levels (each injected in duplicate) was used. Linear regression equations were generated with 1/x weighting, resulting in calibration functions with correlation coefficients of $r > 0.99$.

Calibration functions ranging from 0.025 ng/mL to 5.0 ng/mL (≥5 levels: 0.025, 0.10, 0.50, 1.0, 2.50 and 5.0 ng/mL) were used to quantify Reg. No. 4982164 (P36) recoveries (Figure 5 and Figure 6). For evaluation of the stability in extracts a calibration function ranging from 0.50 ng/mL to 5.0 ng/mL with 3 levels (each injected in duplicate) was used. Linear regression equations were generated with 1/x weighting, resulting in calibration function with correlation coefficient of $r > 0.99$.

Representative LC/MS/MS ion chromatograms of calibration solutions in solvent and diluted sample extracts of fortified and control specimens for pendimethalin, M455H001 and Reg. No. 4982164 (P36) are presented in Figure 9 through Figure 32.

2.4.2 GC/MS/MS Analysis

Pendimethalin metabolite Reg. No. 4061757 was quantitated using the following GC/MS/MS method in the negative chemical ionization (NCI) mode:

GC/MS System	Thermo TSQ Quantum GC/MS System equipped with TriPlus AS autosampler, Trace Ultra GC gas chromatograph, temperature programmable PTV and split/splitless injector, digital pressure and flow control DPFC.
Carrier gas	Helium at 1.5 mL/min (constant flow).
GC Injection technique	Isothermal injection at 250 °C, splitless.
GC Injection Volume	3.0 µL.
GC capillary column	Agilent VF-5MS (30 m length, 0.32 mm inner diameter, 0.25 µm film thickness).
Oven temperature program	50°C, 2 min hold, ramp with 20°C/min to 300°C, 3 min hold.
Ion Source Conditions	Emission current: 120 µA Electron energy: -100 eV CI Gas: Methane with constant flow at 2.0 mL/min Negative Chemical Ionisation
MS Conditions	Selected reaction monitoring (SRM) mode, monitoring the following fragment ions: Reg. No. 4061757: 211 m/z -> 194 m/z used for quantification 211 m/z -> 193m/z used for confirmation. (Q2) Collision Gas Pressure: 1.4 mTorr Collision Energy (CE): 15 eV
Retention time	Reg. No. 4061757: ~ 10 minutes

Figure 44 presents the full scan product ion NCI spectrum of pendimethalin metabolite Reg. No. 4061757 showing the selection of the two structurally significant product ions used for the GC/MS/MS quantification/confirmation and the parent ion.

For Reg. No. 4061757, quantification was carried out by external standardization using calibration standards in solvent. Only for LOQ Bruch West calibration standards in matrix were used for quantification.

Calibration functions ranging from 1.0 ng/mL to 50 or 100 ng/mL (≥ 5 levels: 1.0, 2.5, 5.0, 10, 25, 50 and 100 ng/mL) were used to quantify Reg. No. 4061757 recoveries (Figure 7 and Figure 8). This calibration was preferred compared to matrix based calibration because it is independent from availability of appropriate blank matrix. Linear regression equations were generated with 1/x weighting, resulting in calibration functions with regression coefficients of $r^2 > 0.99$.

Representative GC/MS/MS ion chromatograms of calibration solutions in solvent and of diluted sample extracts of fortified and control specimens for Reg. No. 4061757 are presented in Figure 33 through Figure 40.

2.5 Calculations

2.5.1 LC/MS/MS Analysis for Pendimethalin, M455H001 and Reg. No. 4982164 (P36)

Recovery results and calculations derived from LC/MS/MS analysis of pendimethalin and M455H001 are shown in detail in Table 1 for the Li10 soil and Table 2 for the Bruch West soil.

Recovery results and calculations derived from LC/MS/MS analysis of Reg. No. 4982164 (P36) are shown in detail in Table 5 for the Li10 soil and Table 6 for the Ranschgraben sediment.

The following equation was used to calculate the individual residues R in mg/kg:

$R = c_{End} \times DF \times (V_{Ex}/W)/1000\ ng/\mu g$

$= c_{End} \times M \times DF$

R: Analyte residue in mg/kg.

c_{End}: Concentration of analyte in final sample volume, in ng/mL. (where multiple injections were evaluated: mean).

V_{Ex}: Final extract volume, in mL: 60 mL for soil, 65 mL for sediment extracts

W: Sample weight, in g: 10.0 g

DF: Dilution factor

M: Multiplier

Recoveries (Rec.) were calculated for the fortified specimens as follows:

$Rec. = (R/R_{fortified}) \times 100\%$

The pendimethalin calculation is exemplified with the Li10 soil sample P2768-32 fortified at 0.10 mg/kg (10 x LOQ). The final sample volume was examined by LC/MS/MS in run file P2768#035 (Figure 11) to give a final concentration C_{End} of 1.62 ng/mL for 282 *m/z* -> 194 *m/z*. The following calculation is demonstrated for the fragment ion 194 m/z:

Thus:

$R = c_{End} \times DF \times (V_{Ex}/W)/1000\ ng/\mu g$

$= c_{End} \times DF \times M$

$R = 1.62\ ng/mL \times 10 \times (60\ mL/10\ g)/1000\ ng/\mu g$

$= 1.62\ ng/mL \times 10 \times 0.0060\ (mL/g)/(ng/\mu g)$

$= 0.097\ mg/kg$

$Rec. = (R/R_{fortified}) \times 100\%$

$= (0.097\ mg/kg/0.10\ mg/kg) \times 100\ \% = 97\%$

Calculations were performed with full precision by computer software (Excel). Thus slight discrepancies may arise when using other methods.

2.5.2 GC/MS/MS Analysis for Reg. No. 4061757

Recovery results derived from GC/MS/MS analysis and calculations are shown in detail in Table 3 for the Li10 soil and Table 4 for the Bruch West soil.

The following equation was used to calculate the individual residues R in mg/kg:

$R = c_{End} \times DF \times (V_{Ex}/W)/1000\ ng/\mu g$

$= c_{End} \times M \times DF$

R: Analyte residue in mg/kg.

c_{End}: Concentration of analyte in final sample volume, in ng/mL. (where multiple injections were evaluated: mean).

V_{Ex}: Final extract volume, in mL: 20 mL

W: Sample weight, in g: 10.0 g

DF: Dilution factor, if applicable.

M: Multiplier

Recoveries (Rec.) were calculated for the fortified specimens as follows:

$Rec. = (R/R_{fortified}) \times 100\%$

The Reg. No. 4061757 calculation is exemplified with the Li10 soil sample P2768-67 fortified at 0.10 mg/kg (10 x LOQ). The final sample volume was examined by GC/MS/MS in run file P2768#016 (Figure 35) to give a final concentration C_{End} of 42.83 ng/mL for 211 *m/z* -> 194 *m/z*. The following calculation is demonstrated for the fragment ion 194 m/z:

Thus:

$R = c_{End} \times DF \times (V_{Ex}/W)/1000\ ng/\mu g$

$= c_{End} \times DF \times M$

$R = 42.83\ ng/mL \times 1 \times (20\ mL/10\ g)/1000\ ng/\mu g$

$= 42.83\ ng/mL \times 1 \times 0.0020\ (mL/g)/(ng/\mu g)$

$= 0.086\ mg/kg$

$Rec. = (R/R_{fortified}) \times 100\%$

$= (0.086\ mg/kg/0.10\ mg/kg) \times 100\ \% = 86\%$

Calculations were performed with full precision by computer software (Excel). Thus slight discrepancies may arise when using other methods.

4. CONCLUSION

PTRL Europe successfully performed the method validation in soil and sediment for the determination of pendimethalin (BAS 455 H), M455H001 and Reg. No. 4982164 (P36) by LC/MS/MS and Reg. No. 4061757 by GC/MS/MS, demonstrating an LOQ of 0.010 mg/kg and an LOD of 0.003 mg/kg for all four analytes.

It can be concluded that the residue methods fulfills all requirements as defined in the EC Guidance documents on residue analytical methods (SANCO/825/00, rev. 8.1 (16/11/2010) and SANCO/3029/99, rev. 4 (11/07/00).

In addition, it was demonstrated that pendimethalin and its three metabolites are stable in sample extracts for at least 4 days under both refrigerated and frozen storage conditions.

1. INTRODUCTION

Background and Objective:

Upon request of the Sponsor, the study with report finalized on 18-Apr-13 was resumed by amendment to validate the analytical method for the determination of pendimethalin in soil with an improved target limit of quantitation (LOQ) of 1.0 µg/kg.

2. EXPERIMENTAL

2.1 Test System and Analytical Test/Reference Item

The same soils as employed throughout the study were used.

2.2 Analytical Test and Reference Items

The same pendimethalin analytical standard as employed throughout the study was used.

2.3 Analytical Method

The same solvents, chemicals, equipment and LC/MS/MS instrumentation as employed throughout the study were used.

Solutions were prepared as described in detail in the initial study report.

Additionally, due to the 10-times higher concentration of soil co-extracted matter, matrix-matched standards were prepared, using soil extracts from untreated soil blank samples. The concentrations prepared by volumetric dilutions were in a range from 0.025 to 5.0 ng/mL. Therefore e.g. 1900 µL of untreated soil blank extract was fortified with 100 µL of standard solution containing Pendimethalin at a concentration of 100 ng/mL resulting in a final concentration of Pendimethalin of 5.0 ng/mL. Followed by further dilution in blank soil extract.

Soil extraction and final extract preparation for pendimethalin was done as described in detail in the initial study report with the exception that the final dilution step (DF = 10) was avoided.

2.4 LC/MS/MS Analysis

Pendimethalin (BAS 455 H) was quantified using the same LC/MS/MS method as before.

Now, however, with improved LOQ, pendimethalin determination was carried using calibration standards in matrix.

Calibration functions ranging from 0.025 ng/mL to 5.0 ng/mL (≥ 5 levels: 0.025, 0.10, 0.50, 1.0 and 5.0 ng/mL) were used to quantify pendimethalin (Figure 1 through Figure 4). Linear regression equations were generated with 1/x weighting, resulting in calibration functions with correlation coefficients of $r > 0.99$.

Representative LC/MS/MS ion chromatograms of calibration solutions in matrix and sample extracts of fortified and control specimens for pendimethalin are presented in Figure 5 through Figure 10.

2.5 Calculations

Pendimethalin (BAS 455 H) results calculation was done as described before.

Recovery results and calculations derived from LC/MS/MS analysis of pendimethalin are shown in detail in Table 1.

Calculations were performed with full precision by computer software (Excel). Thus slight discrepancies may arise when using other methods.