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GRM022.02A

Dicamba: Residue Method for the Determination of Residues in Water

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DATA REQUIREMENT: EPA OPPTS 850.7100
EC Guidance Document SANCO/3029/99 rev 4
EC Guidance Document SANCO/825/00 rev 7

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Summary of revisions to previous version

Version	Summary of Revisions
	New method

Authorisation

Authorised by : S Hadfield

S Hadfield
Manager
Product
Metabolism

5th Oct 2007
Date

Abbreviations and symbols

Abbreviation	Definition
A	acre
a.i.	active ingredient
amt	amount
amu	atomic mass unit
C	Celsius or Centigrade
CAS	Chemical Abstract Services
CFR	Code of Federal Regulations
cm	centimeter
DA[#]A	days after application, [#] = 1, 2, 3 etc., if there are multiple applications
EPA	Environmental Protection Agency (U.S.)
EU	European Union
FIFRA	Federal Insecticide, Fungicide and Rodenticide Act (U.S.)
ft	foot (feet)
G	gram
gal	gallon
GC	gas chromatography
GLP	Good Laboratory Practice
GRM	Global Residue Method
ha	hectare
HPLC	high performance liquid chromatography
i.d.	inside diameter
ID	identification
in	inch
IUPAC	International Union of Pure and Applied Chemistry
kg	kilogram
L	liter
lb	pound
LC	liquid chromatography
LC-MS/MS	tandem liquid chromatography/mass spectrometry/mass spectrometry
LOD	limit of detection
LOQ	limit of quantitation
m	meter

Abbreviations and symbols (continued)

Abbreviation	Definition
µg	microgram
µL	Microliter
µm	Micrometer
MDL	method detection limit
mg	Milligram
mL	Millilitre
mm	Millimetre
mmol	Millimole
min	minute
mol	Mole
MS	mass spectrometry
MS/MS	tandem mass spectrometry/mass spectrometry
ms	Millisecond
mV	Millivolt
MW	molecular weight
m/z	mass to charge ratio
n/a	not applicable
ND or nd	Not detectable (below limit of detection)
ng	Nanogram
No.	Number
oz	Ounce
PMRA	Pest Management Regulatory Agency, Canada
ppb	parts per billion or micrograms per kilogram
ppm	parts per million or microgram per gram or milligrams per kilogram
pg	Picogram
psi	pounds per square inch
QAU	quality assurance unit
R^2 (or r^2)	square of correlation coefficient
RSD	relative standard deviation
Rt	retention time
s	Second
SD	standard deviation
SPE	Solid Phase Extraction

Abbreviations and symbols (continued)

Abbreviation	Definition
USDA	United States Department of Agriculture
UV	Ultraviolet
V	Volt
vol	Volume
wt	Weight

TABLE OF CONTENTS

1.0 INTRODUCTION

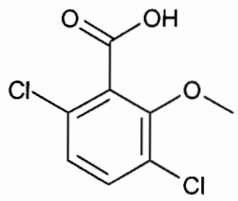
Scope and chemical structures

Analytical method GRM022.02A is suitable for the determination of dicamba (Figure 1) in water using an external standardisation procedure. The limit of quantitation (LOQ) of the method is 0.05 μg L^{-1}.

This method satisfies EU guidelines SANCO/3029/99 rev. 4, SANCO/825/00 rev. 7 and US EPA guideline OPPTS 850.7100.

Figure 1

Compound Code Number	:	SAN837
Common Name	:	dicamba
CAS Number	:	1918-00-9
IUPAC Name	:	3,6-dichloro-*o*-anisic acid
Molecular Formula	:	$C_8H_6Cl_2O_3$
Molecular Mass	:	221.0



1.2 Method summary

Acidified water samples are passed through C18 solid phase extraction (SPE) cartridges. Dicamba is eluted from the SPE cartridge with acetonitrile. Aliquots are derivatised to form the tert-butyl dimethylsilyl ester using *N*-(*tert*-Butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA). Final determination is by negative-ion chemical ionisation gas liquid chromatography with mass selective detection (NICI GC-MSD). The limit of quantification of the method is 0.05 μg L^{-1}.

2.0 MATERIALS AND APPARATUS

2.1 Apparatus

The recommended equipment and apparatus are listed in Appendix 1. Equipment with equivalent performance specifications may be substituted.

2.2 Reagents

All solvents and other reagents must be of high purity, e.g. glass distilled/HPLC grade solvents and analytical grade reagents. Particular care must be taken to avoid contamination of the reagents used. Reagents of comparable purity may be substituted as long as acceptable performance is demonstrated. A list of reagents used in this method is included in Appendix 2.

2.3 Preparation of analytical standard solutions

It is recommended that the following precautions should be taken when weighing the analytical materials.

1. Ensure good ventilation.
2. Wear gloves and laboratory coat.
3. Prevent inhalation and contact with mouth.
4. Wash any contaminated area immediately.

Prepare a 200 $\mu g\ mL^{-1}$ stock solution for dicamba by one of the following methods.

Weigh out accurately, using a five figure balance, sufficient dicamba analytical standard and carefully transfer into separate "Class A" volumetric flasks (50 mL). Dilute to the mark with acetone to give a 200 $\mu g\ mL^{-1}$ stock solutions of dicamba.

Alternatively, the appropriate volume of acetone to add to a known amount of standard material may be determined using the equation below. The standard concentration is corrected for its chemical purity.

$$V = \frac{W \times P}{C} \times 1000$$

P = Standard purity in decimal form (P(%)/100)
V = Volume of acetone required
W = Weight, in mg, of the solid analytical standard
C = Desired concentration of the final solution, ($\mu g\ mL^{-1}$)
1000 = Unit conversion factor

The standard material is weighed into a "Class A" volumetric flask.

Sample fortification solutions should be prepared in acetone from the primary stock solution in "Class A" volumetric flasks. It is recommended that, as a minimum, the following solutions are prepared by serial dilution: 10 μg mL^{-1}, 1.0 μg mL^{-1}, 0.1 μg mL^{-1} and 0.01 μg mL^{-1}. The preparation of GC-MSD calibration standards is discussed in Section 3.4.

All stock solutions should be stored in a refrigerator or freezer when not in use to prevent decomposition and/or concentration of the standard. Standard solutions should be allowed to equilibrate to room temperature prior to use.

An expiration date of six months is recommended unless additional data are generated to support a longer or shorter expiration date.

2.4 Safety precautions and hazards

The following information is included as an indication to the analyst of the nature and hazards of the reagents used in this procedure. If in any doubt, consult the appropriate MSDS or a monograph such as 'Hazards in the Chemical Laboratory', edited by S G Luxon, The Chemical Society, London (Reference 1).

Reagent hazards

	Acetone	Methanol	Acetonitrile	Hydrochloric acid	MTBSTFA
Harmful Vapour	✓	✓	✓	✓	✓
Highly Flammable	✓	✓	✓	×	✓
Harmful by Skin Absorption	×	×	✓	✓	✓
Irritant to eyes and respiratory tract, causes burns	×	×	×	✓	×
Syngenta Divisional Toxicity Class	SHC D, S	SHC C, S	SHC C, S	SHC-C, S	SHC-C, S
OES Short Term (mg m^{-3})	3560	310	105	7	N/A*
OES Long Term (mg m^{-3})	1780	260	70	N/A*	N/A*

*N/A not known.

In all cases avoid breathing vapour. Avoid contact with eyes and skin.

Dicamba has been assigned to Syngenta Hazard Classification (SHC) C, S. The toxicity classification scale rates highly toxic chemicals as class E and non toxic chemicals as class A. An additional hazard category of S indicates the compound is a severe skin and eye irritant.

3.0 ANALYTICAL PROCEDURE

The method is summarized in flow chart form in Appendix 7.

3.1 Sample Preparation

a) If water samples are received frozen, they should be allowed to defrost thoroughly at room temperature before analysis. Once completely thawed the bulk water samples should be shaken thoroughly prior to analysis.

b) Transfer 50 mL of the water sample to be analysed into a polypropylene centrifuge tubes (50 mL size). Sample fortification, if required, is to be carried out at this point. At least one untreated control and two control samples fortified with a known amount of dicamba in acetone should be analysed alongside each batch of samples to demonstrate acceptable performance of the method and allow recovery corrections to be made if desired. Recovery samples should be fortified at the level expected in the samples.

c) Add concentrated hydrochloric acid (200 µL) to each sample. Cap the tubes securely and shake gently to mix.

3.2 Solid Phase Extraction Procedure

a) Take one IST C18 SPE cartridge (100 mg, 10 mL) for each sample to be analysed and place on a suitable vacuum manifold (e.g. IST Vacmaster). Add methanol (2 mL) and allow to percolate through under gravity or draw through under vacuum to the level of the top frit at a rate of approximately 1 mL min^{-1}, discarding the column eluate. Do not allow the cartridges to become dry. Add ultra pure water (2 mL) to the top of each cartridge and allow to percolate through under gravity or draw through under vacuum to the level of the top frit at the same rate, again discarding the column eluate. Do not allow the cartridges to become dry.

b) Carefully transfer water samples from Section 3.1 (c) onto the SPE cartridges and allow to percolate through under gravity or under low vacuum, at a rate of approximately 1-2 mL min^{-1}, to the level of the top frit. Do not allow cartridges to become dry during this process.

c) On completion of sample loading, remove any droplets of water adhering to the sides of the SPE cartridges using clean absorbent tissue. Dry cartridges under high vacuum (< 500 m bar) for 15 minutes. Where such vacuum is not achievable, longer drying times may be required.

Note: It is important that the cartridges are completely dry before elution. Any remaining water on the cartridge may have an adverse effect on the derivatisation process and accurate quantification will be compromised.

d) Place suitable plastic graduated disposable collection tubes (e.g. 15 mL size) under each port, as required, in the manifold rack. Elute cartridges with acetonitrile (2 mL), under gravity or draw through under low vacuum at a rate of approximately 1-2 mL min^{-1} to the level of the top frit collecting the column eluate. Apply positive pressure or high vacuum for approximately 5 seconds to collect the excess solvent from the SPE cartridges.

Note: The above SPE procedure has been developed using columns from the stated manufacturer, however, it is possible to carry out the procedure using similar columns from other manufacturers. In all cases, it is strongly recommended that the elution profile of the chosen batch of columns is checked prior to commencing analysis to rule out any variation between manufacturers' products and between batches.

e) Adjust final volume to 2 mL with acetonitrile. Mix thoroughly by securing caps and shaking gently. The final sample concentration is 25 mL mL^{-1}.

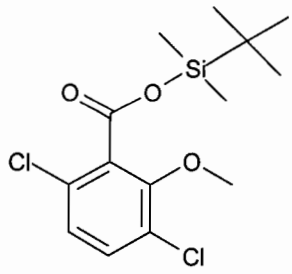
f) Transfer aliquots 1 mL into suitable autosampler vials for derivatisation.

3.3 Derivatisation Procedure

a) Add MTBSTFA (100 µL) to each sample from 3.2 (f) and crimp vials securely. Shake gently to mix and heat at 60 °C for 15 minutes in a suitable heating block. Samples are now ready for final determination by NICI GC-MSD. The structure of derivatised dicamba is shown below (Figure 2).

Figure 2

Compound	:	Dicamba *tert*-butyl dimethylsilyl ester
CAS Number	:	Not in registry
Molecular Formula	:	$C_{14}H_{20}Cl_2O_3Si$
Molecular Mass	:	335.14



3.4 Preparation of GC-MSD Calibration Standard

Enhancement of the instrument response for dicamba has been observed in the water types tested using the above procedure in this laboratory. It is recommended that matrix effects are

determined prior to analytical water sample analysis to determine whether non-matrix standards are suitable for analyses. Calibration standards should be prepared as described below.

To prepare a 0.001 μg mL^{-1} calibration standard, transfer 100 μL of a 0.1 μg mL^{-1} dicamba in acetone to a 10 mL volumetric flask. Adjust to the mark with acetonitrile or control sample solution (from section 3.2 e), in the case of matrix matched standards. Stopper securely and shake to mix thoroughly. Transfer a 1 mL aliquot of the standard in acetonitrile to a suitable autosampler vial for derivatisation. Derivatise as described in Section 3.3 for analysis by NICI GC-MSD.

A calibration curve may also be generated to quantify dicamba residues. Derivatised standards over the concentration range 0.625-50 ng mL^{-1} should be prepared as described above, using appropriate amounts of dicamba standard in acetone

3.5 Time required for analysis

The methodology is normally performed with a batch of 20 or more samples. One person can complete the analysis of 20 samples in 0.5 day (8 hour working period).

3.6 Method stopping points

The analytical procedure can be stopped at various points for overnight and weekend breaks unless otherwise specified in the analytical procedure. It is recommended however, that analyses are performed on the day of preparation. Acceptable method recoveries will validate any work flow interruptions. Samples should be stored refrigerated in sealed containers where the analysis cannot be completed in a single day.

4.0 FINAL DETERMINATION

The following instrument and conditions have been found to be suitable for this analysis in this laboratory. Other instruments can be equally used, however optimisation may be required to achieve the desired separation and sensitivity. The operating manuals for the instruments should always be consulted to ensure safe and optimum use.

This method has been developed for use on an Agilent 5973 mass selective detector instrument, with an Agilent 6890 series GC system operating in negative ion chemical ionisation mode.

Instrument description.

Chromatography conditions

Column	:	Varian CPSIL-8 (30.0 m x 0.25 mm i.d., df = 0.25 μm)
Injection Port	:	Splitless with silanised glass wool plug
Carrier gas and head pressure	:	Helium at 1.0 mL min^{-1} constant flow
Injection mode	:	Pulsed (pulse pressure 30.0 psi)

Purge Time	:	2 min
Purge Flow	:	50 mL/min
Injection volume	:	1 μL
Injector temperature	:	275°C
Detector temperature	:	300°C
Transfer line temperature	:	280°C
Ion source temperature	:	150°C
Quadrupole temperature	:	106°C
Temperature programme	:	60°C (hold for 1 minute), 20°C min^{-1} to 300°C (hold for 1 minute).
MSD Conditions		
Mode	:	Negative CI
Reagent gas	:	Methane
Electron energy	:	Maximum 230 eV (set by autotune)
System Calibration	:	Autotune

Acquisition Parameters

Compound Name	Low Mass Resolution	SIM	MODE
Dicamba	Yes	Target Ion	184 *m/z*
		Qualifier 1	185 *m/z*
		Qualifier 2	186 *m/z*
		Retention Time	10.2 mins

Final determination is by NICI GC-MSD monitoring 3 ions with $m/z \geq 100$. This is considered to be highly specific; hence no confirmatory conditions are included. Quantification may be carried out on any of the above ions. Typical chromatograms are shown in Appendix 4. The full scan spectrum showing the fragmentation of dicamba is included in Appendix 6.

5.0 CALCULATION OF RESULTS

Residues may be calculated using an external standardisation procedure. Dicamba residues may be calculated in $\mu g\ L^{-1}$ for each sample using a mean standard response from each of the injections bracketing the sample as follows.

5.1 Single point calibration procedure

a) Make repeated injections of a standard containing dicamba at an appropriate concentration into the GC-MSD operated under conditions as described in Section 4. When a consistent response is obtained, measure the peak areas obtained for dicamba.

b) Make an injection of each sample solution and measure the peak areas of the peaks corresponding dicamba.

c) Re-inject the standard solution after a maximum of four injections of sample solutions.

d) Calculate the dicamba residues in the sample, expressed as $\mu g\ L^{-1}$, using a mean standard response from each of the injections bracketing the sample as follows.

$$\text{Residue concentration} = \frac{\text{PK area(SA)}}{\text{PK area(STD)}} \times \frac{\text{Standard Conc.}}{\text{Sample Conc.}}$$

PK area (SA) = Peak response for sample
PK area (STD) = Average peak response for bracketing standards
Standard Conc. = Concentration of standard ($\mu g\ mL^{-1}$)
Sample Conc. = Sample concentration ($L\ mL^{-1}$)

If residues need to be corrected for average percentage recovery, then the equation below should be used.

$$\text{Corrected Residue concentration} = \frac{\text{Residue} \times 100}{\text{Average percentage Recovery}}\ (\mu g\ L^{-1})$$

When the average percentage recovery is greater than 100%, the sample residue values should not be corrected.

5.2 Multi point calibration procedure

Dicamba residues may be calculated in $\mu g\ L^{-1}$ for each sample as follows.

a) Prepare standard solutions over a concentration range appropriate to the expected residues in the samples (for example, 50% LOQ to 10 x LOQ). An appropriate number of different concentrations within this range should be prepared (at least four).

b) Make an injection of each sample solution and measure the areas of the peaks corresponding to dicamba. Calibration standard solutions should be interspersed throughout the analysis, after a maximum of four injections of sample solutions.

c) Generate calibration curve parameters using an appropriate regression package.

d) The following equation can be rearranged and used to calculate residues as follows:

$$y = mx + c$$

Where y is the instrument response value, x is the standard concentration, m is the gradient of the line of best fit ("X-variable 1" in MS Excel) and c is the intercept value. An example of this equation generated using the experimental values of m and c should be included in the raw data, as should the "R-Squared" value for the regression. Re-arrangement for x gives

$$x = \frac{y - c}{m}$$

e) Alternatively (depending on the regression analysis software available) a quadratic equation may be used to fit the data. In this case the following general equation should be re-arranged and used to calculate residues:

$$y = a + bx + cx^2$$

Where y is the instrument response value, x is the standard concentration and a, b, c are constants.

f) Calculate the dicamba residues in the sample, expressed as $\mu g\ L^{-1}$, as follows

$$\text{Residue concentration } (\mu g\ L^{-1}) = \frac{\text{Analyte found } (\mu g\ mL^{-1})}{\text{Sample conc. } (L\ mL^{-1})}$$

Where analyte found ($\mu g\ mL^{-1}$) is calculated from the standard calibration curve and sample conc. is the final sample concentration in $L\ mL^{-1}$.

If residues need to be corrected for average percentage recovery, then the equation below should be used.

$$\text{Corrected Residue concentration} = \frac{\text{Residue} \times 100}{\text{Average percentage Recovery}} (\mu g\ L^{-1})$$

When the average percentage recovery is greater than 100%, the sample residue values should not be corrected.

6.0 CONTROL AND RECOVERY SAMPLES

Control water samples should be completed as detailed in Sections 3.1-3.3 for each set of samples analysed to verify that the sorbent is free from dicamba contamination. A minimum of one control should be analysed with each batch of samples.

At least two recovery experiments (untreated water samples accurately fortified with a known amount of dicamba prior to extraction) should also be completed alongside each batch of samples. Provided the recovery values are acceptable they may be used to correct any dicamba residues found. The recovery levels should be appropriate to the residue levels expected.

Recovery data is generally considered acceptable when the mean values are between 70% and 110% and with a relative standard deviation of $\leq$20%

7.0 SPECIFICITY

It is recommended that reagent blank samples be included in a sample set if contamination is suspected.

7.1 Matrix Interference

Enhancement of the GC-MSD signal caused by the water matrices has been observed for all the water samples tested. It is recommended that matrix effects are determined prior to analytical water sample analysis to determine whether non-matrix standards are suitable for analyses.

7.2 Reagent and solvent interference

Using high purity solvents and reagents no interference has been found.

7.3 Labware interference

This method uses mainly disposable labware. It is recommended that the use of reusable labware should be avoided but if used then all reusable glassware should be detergent washed and rinsed with HPLC grade methanol, acetone or acetonitrile prior to use.

8.0 METHOD VALIDATION

8.1 Recovery data and repeatability

Method validation has been carried out on the procedures described in Section 3.0. The method validation data is reported in T002102-06-REG (Reference 2), and a summary is included in Appendix 3.

8.2 Limit of quantitation (LOQ)

The limit of quantitation of the method is defined as the lowest analyte concentration in a sample at which the methodology has been validated and a mean recovery of 70-110% with a relative standard deviation of $\leq$ 20% has been obtained. Generally, for accurate quantitation, the response for an analyte peak should be no lower than four times the mean amplitude of the background noise in an untreated sample at the corresponding retention time.

The limit of quantitation has been set at 0.05 $\mu g\ L^{-1}$.

8.3 Limit of detection (LOD)

The limit of detection of the method is defined as the lowest analyte concentration detectable above the mean amplitude of the background noise in an untreated sample at the corresponding retention time. An estimate of the LOD can be taken as three times background noise. Note that the LOD may vary between runs and from instrument to instrument.

The limit of detection for this procedure in the water tested is estimated at 0.008 to 0.014 μg L^{-1} for dicamba using the target ion *m/z* = 184, 0.007 to 0.014 μg L^{-1} using qualifier ion *m/z* = 185 and 0.008 to 0.014 μg L^{-1} using qualifier ion *m/z* = 186.

8.4 Detector linearity

For accurate quantitation of residue concentrations, analyses should be carried out within the linear range of the detector. Detector linearity graphs are given in Appendix 5.

In these laboratories the linearity of the NICI GC-MSD detector response for dicamba was tested in the range from 0.625 ng mL^{-1} to 50 ng mL^{-1} (equivalent to 0.625 pg to 50 pg injected on column when using a 1 μL injection volume) and was found to be linear. If a residue beyond the tested concentration range is expected, dilute the extract appropriately to bring it within the tested linear range prior to quantitation.

Standards at 5 different concentration levels (n = 5) were injected in triplicate and the mean response plotted against amount injected, using Microsoft Excel 2003. The intercept was set to zero and a linear trendline fit applied. The data were also plotted with no intercept set. The two plots were compared statistically by application of a t-test, performed using Microsoft Excel 2003. t-values of 1.447 for the target ion *m/z* = 184 3.089 for the qualifier ion *m/z*= 185 and 2.235 for the qualifier ion *m/z*= 186 were obtained for dicamba with n – 2 (= 3) degrees of freedom. The tabular t value at the 5% level of significance, with n – 2 (= 3) degrees of freedom, is 3.182. Since the computed t values are smaller than the tabular t value, at the 5% level of significance, the intercept α is not significantly different from zero and the two response curves are statistically similar. It is therefore acceptable to use single point calibrations for residue calculations (Reference 3).

8.5 Extract stability

Stability of final extracts of derivatised dicamba samples has not been performed. It is recommended that analyses are performed on the day of preparation. Acceptable method recoveries will validate any work flow interruptions. Samples should be stored refrigerated in sealed containers where the analysis cannot be completed in a single day.

9.0 LIMITATIONS

The method has been tested on representative water types. It can reasonably be assumed that the method can be applied to other water sources not tested in this method provided successful recovery tests at the relevant levels validate the suitability of the method.

10.0 CONCLUSIONS

This procedure has been demonstrated to be a reliable and accurate procedure for the determination of dicamba residues in water. Only commercially available laboratory equipment

and reagents are required. The analysis of a batch of 20 samples can be completed by one person in 0.5 day (8 working hour period). Untreated and fortified samples should be analysed with each set of samples to demonstrate absence of any interference and adequate recovery, if possible. The limit of quantitation of the method is 0.05 $\mu g\ L^{-1}$.

This method complies with EU guidelines SANCO/3029/99 rev. 4, SANCO/825/00 rev. 7 and US EPA guideline OPPTS 850.7100.

11.0 REFERENCES

1. Luxon S G (1992): Hazards in the Chemical Laboratory 5th Edition. The Royal Society of Chemistry. Thomas Graham House, The Science Park, Cambridge CB4 4WF, UK. ISBN 0-85186-229-2.

2. Emburey S N (2007). Dicamba - Validation of an Analytical Method for the Determination of Residues of Dicamba in Water. T002102-06-REG.

3. Cardone M J, Palermo P J and Sybrand L B : Potential error in single point ratio calculations based on linear calibration curves with a significant intercept. Anal Chem., 52 pp 1187-1191, 1980

APPENDICES SECTION

APPENDIX 1 APPARATUS

UK suppliers

General laboratory glassware, available from Fisher Scientific UK, Bishop Meadow Road, Loughborough, Leicestershire LE11 5RG, UK

Polypropylene centrifuge tubes, 50 and 15 mL capacity. Available from Fisher Scientific UK, Bishop Meadow Road, Loughborough, Leicestershire LE11 5RG, UK.

Isolute® Vacmaster-20® sample processing station, available from Argonaut Technologies, Tir-y-Berth Industrial Estate, New Road, Hengoed, Mid Glamorgan CF8 8AU, UK.

IST C18 solid phase extraction cartridges 100 mg, 10 mL size, available from Argonaut Technologies, Tir-y-Berth Industrial Estate, New Road, Hengoed, Mid Glamorgan CF8 8AU, UK.

Crimp cap auto sampler vials and caps available from Agilent Technologies UK Limited, Chemical Analysis Group, Lakeside Heath, Cheadle Royal Business Park, Stockport, Cheshire, SK8 3GR, UK.

Techne Dri-block 3D heating block, available from Fisher Scientific UK, Bishop Meadow Road, Loughborough, Leicestershire LE11 5RG, UK.

Agilent 5973 MSD system equipped with an Agilent 6890 GC system and Agilent 7683 autosampler injector system, available from Agilent Technologies UK Ltd. , Lakeside, Cheadle Royal Business Park, Stockport, Cheshire SK8 3GR.

GC column, Varian CP-SIL 8 CB (5% phenyl 95% dimethlypolysiloxane), available from Varian Ltd. , 28 Manor Road, Walton-on Thames, Surrey KT12 2QF.

Double gooseneck injection liner 4 mm i.d. for HP splitless injectors, available from Thames chromatography, Fairacres Industrial Centre, Dedworth Road, Windsor Berkshire, SL4 4LE.

Deactivated glass wool, available from Thames chromatography, Fairacres Industrial Centre, Dedworth Road, Windsor Berkshire, SL4 4LE

US suppliers

General laboratory glassware, available from Fisher Scientific, Liberty Lane, Hampton, NH 03842, USA

Polypropylene centrifuge tubes, 50 mL and 15 mL capacity available from Fisher Scientific, Liberty Lane, Hampton NH 03842, USA

Isolute® Vacmaster-20® sample processing station, available from Argonaut Technologies - Order Processing, 1101 Chess Drive, Foster City, CA 94404

IST C18 solid phase extraction columns 100 mg, 10 mL size, available from Argonaut Technologies - Order Processing, 1101 Chess Drive, Foster City, CA 94404

Crimp cap auto sampler vials and caps available from Agilent Technologies, 395 Page Mill Road, Palo Alto, CA 94304, USA.

Techne Dri-Block heating block used for sample evaporation and derivatisation, available from Techne Incorporated, 3700 Brunswick Pike, Princeton, New Jersey.

Agilent 5973 MSD system equipped with an Agilent 6890 GC system and Agilent 7683 autosampler injector system, available from Agilent Technologies, 395 Page Mill Road, Palo Alto, CA 94304, USA.

GC column, Varian CP-SIL 8 CB (5% phenyl 95% dimethlypolysiloxane), available from Varian Inc. , 2700 Mitchell Drive, Walnut Creek, CA 94598, USA.

Double gooseneck injection liner 4 mm i.d. for HP splitless injectors, available from Restek Corporation, 110 Benner Circle, Bellafonte, PA 168230.

Deactivated glass wool, available from Restek Corporation, 110 Benner Circle, Bellafonte, PA 168230.

APPENDIX 2 REAGENTS

UK suppliers

Solvents: Acetone, methanol and acetonitrile from Rathburn Chemicals Ltd., Walkerburn, Scotland
EH43 6AU

Hydrochloric acid available from e.g. www.sigmaaldrich.com

N-(*tert*-Butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA), available from www.sigmaaldrich.com

Dicamba analytical standard, available from GLP Testing Facility E2A, Syngenta, CH-4333, Munchweilen, Switzerland.

US Suppliers

Solvents: Acetone, methanol and acetonitrile, available from B & J Brand Solvents, from Scientific Products Division of Baxter Healthcare Corporation, USA

Hydrochloric acid available from e.g. www.sigmaaldrich.com

N-(*tert*-Butyldimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA), available from www. sigmaaldrich.com

Dicamba analytical standard, available from Syngenta Crop Protection, Inc., P.O. Box 18300, Greensboro, NC 27419-8300.

APPENDIX 3 METHOD VALIDATION DATA

Table 1 : Dicamba Recovery Data Obtained During Method Validation (Target Ion *m/z* = 184)

Water type	Fortification Level ($\mu g\ L^{-1}$)	Recovery (%)	Mean (%)	RSD (%)	Range
River water	Control	< LOQ, < LOQ			
	0.05*	85, 88, 102, 89, 98	92	8	85 - 102
	0.5	84, 91, 101, 92, 101	94	8	84 - 101
		Overall	93	7	84 - 102
Groundwater	Control	< LOQ, < LOQ			
	0.05*	105, 125, 112, 91, 93	105	13	91 - 125
	0.5	94, 78, 83, 82, 75	83	9	75 - 94
		Overall	94	17	75 - 125
Drinking water	Control	< LOQ, < LOQ			
	0.05*	94, 103, 89, 110, 100	99	8	89 - 110
	0.5	102, 88, 100, 94, 101	97	6	88 - 102
		Overall	98	7	88 - 102

* Limit of quantification, defined by the lowest validated fortification level.

Table 2 : Dicamba Recovery Data Obtained During Method Validation (Qualifier Ion *m/z* = 185)

Water type	Fortification Level ($\mu g\ L^{-1}$)	Recovery (%)	Mean (%)	RSD (%)	Range
River water	Control	< LOQ, < LOQ			
	0.05*	85, 82, 96, 86, 96	89	7	82 - 96
	0.5	83, 89, 103, 93, 103	94	10	83 - 103
		Overall	92	9	82 - 103
Groundwater	Control	< LOQ, < LOQ			
	0.05*	120, 105, 118, 96, 86	105	14	86 - 120
	0.5	88, 78, 79, 79, 78	80	5	78 - 88
		Overall	93	18	78 - 120
Drinking water	Control	< LOQ, < LOQ			
	0.05*	79, 103, 94, 94, 103	95	10	79 - 103
	0.5	85, 83, 91, 78, 85	85	6	78 - 85
		Overall	90	10	78 - 103

* Limit of quantification, defined by the lowest validated fortification level.

Table 3 : Dicamba Recovery Data Obtained During Method Validation (Qualifier Ion *m/z* = 186)

Water type	Fortification Level ($\mu g\ L^{-1}$)	Recovery (%)	Mean (%)	RSD (%)	Range
River water	Control	< LOQ, < LOQ			
	0.05*	77, 84, 94, 79, 93	85	9	77 - 94
	0.5	81, 84, 93, 89, 95	88	7	81 - 95
		Overall	87	8	77 - 95
Groundwater	Control	< LOQ, < LOQ			
	0.05*	104, 93, 83, 103, 81	93	12	81 - 104
	0.5	81, 70, 64, 68, 64	69	10	64 - 81
		Overall	81	18	64 - 104
Drinking water	Control	< LOQ, < LOQ			
	0.05*	86, 94, 92, 110, 86	94	11	86 - 110
	0.5	74, 75, 87, 74, 81	78	7	74 - 87
		Overall	86	13	74 - 110

* Limit of quantification, defined by the lowest validated fortification level.

Determination of GC-MSD matrix effects

The effect of the water types tested on the GC-MSD response may be assessed by preparing standards in the presence of water matrices and comparing the peak areas of dicamba against non-matrix standards at an equivalent concentration.

0.5 $\mu g\ mL^{-1}$ matrix-matched standards were prepared by taking an extra control sample through the procedure as described to point 3.2 (e). An 0.950 mL aliquot was transferred into suitable autosampler vial and 50 μL of 0.01 $\mu g\ mL^{-1}$ dicamba in acetone was added. MTBSTFA (100 μL) was added and the vial realed securely with a crimp cap. The sample was heated at 60 °C for 15 mins to form the dicamba *tert*-butyl-dimethyl silyl ester as described in Section 3.3.

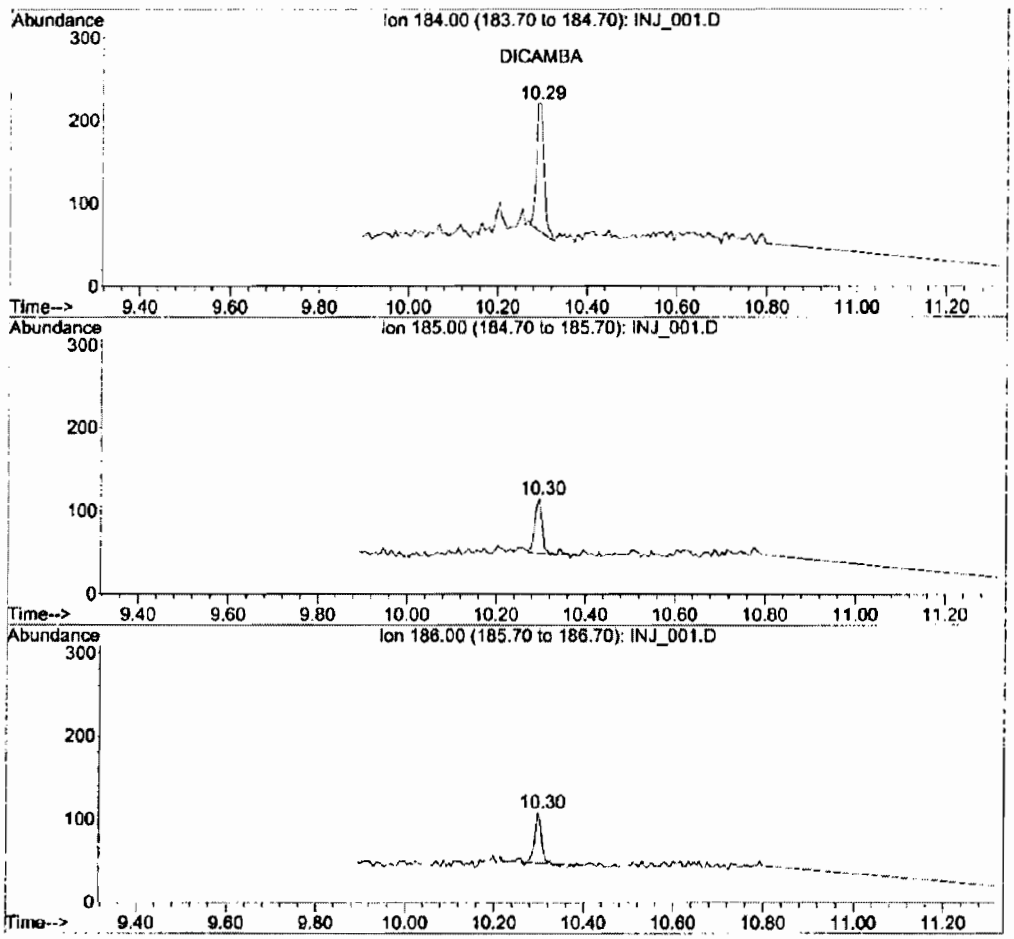
In the validation study, acceptable procedural recovery data was obtained using non-matrix standards for the river and groundwater samples. For drinking water, acceptable procedural recovery data was obtained using matrix matched standards. It is recommended that matrix effects are determined prior to all analytical water sample analysis to determine whether non-matrix standards are suitable for analyses

Table 4 : Matrix Effects

Water type	Matrix Effect for Dicamba		
	Target Ion $m/z = 184$	Confirmatory Ion $m/z = 185$	Confirmatory Ion $m/z = 186$
River water	18.5 % Enhancement	24.9 % Enhancement	14.5 % Enhancement
Groundwater	16.0 % Enhancement	20.2 % Enhancement	5.2 % Enhancement
Drinking water	14.9 % Enhancement	9.4 % Enhancement	20.6 % Enhancement

APPENDIX 4 REPRESENTATIVE CHROMATOGRAMS

Figure 3 : 0.5 μg mL^{-1} Dicamba Standard.
Target Ion *m/z* = 184

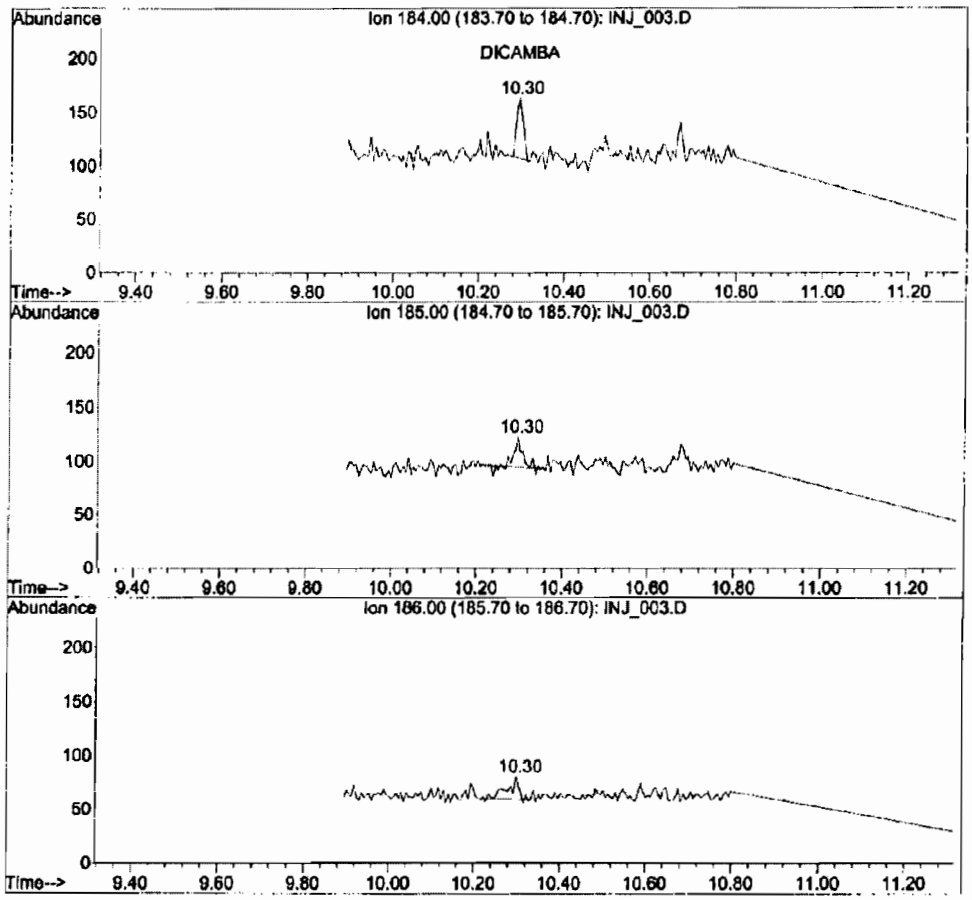


File	: C:\MSDCHEM\1\DATA\062043\INJ_001.D		
Sample Name	: 06-2043/1	Type	: Standard
Field Name	:		

Study Number	: T002102-06	Operator	: Katherine White
Sequence File	: T1439.S	Method File	: TNEGDIC.M
		Vial	: 1
Date Acquired	: 19 Oct 2006 18:37	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.29	1738.8	100
	185	10.30	718.6	41
	186	10.30	747.7	43

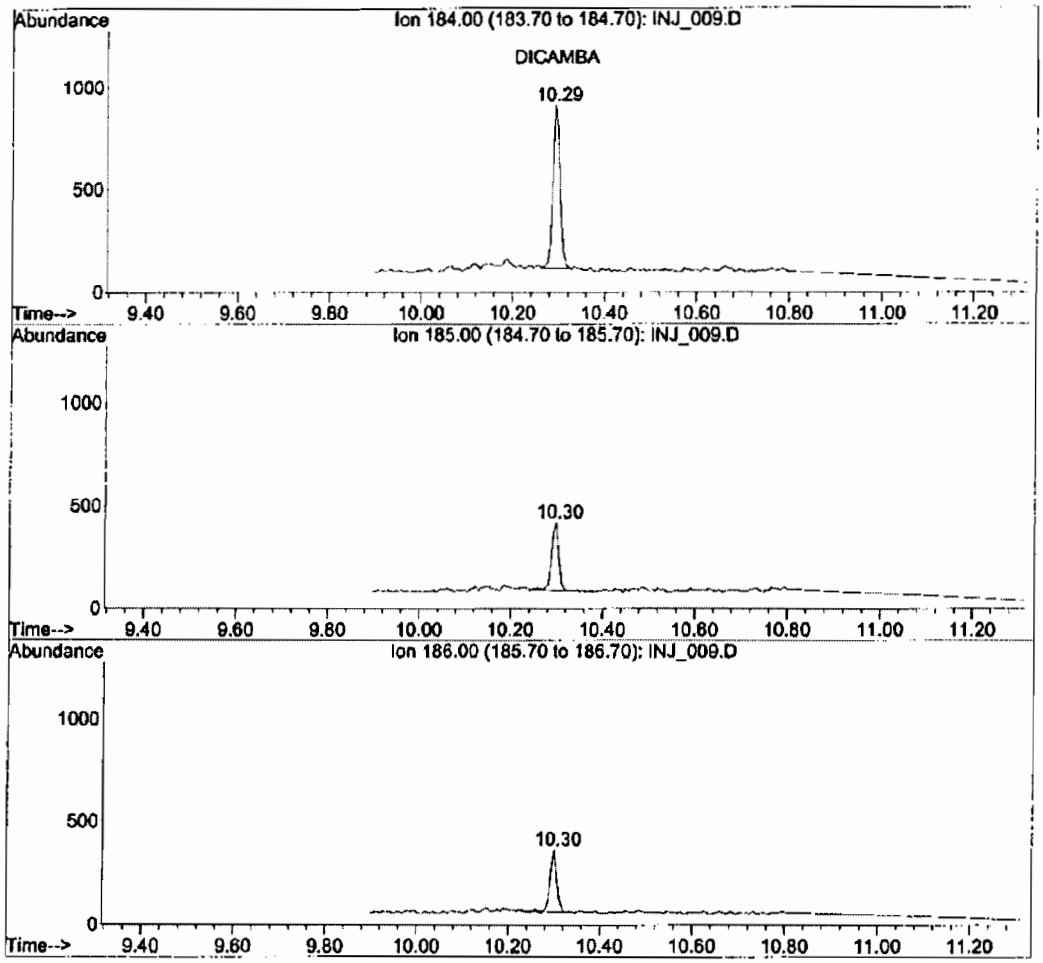
Figure 4 : **River water : Unfortified.**
Sample concentration 25 mL mL^{-1}.Target Ion *m/z* = 184
Residue <LOQ



File	: C:\MSDCHEM\1\DATA\062017\INJ_003.D		
Sample Name	: 06-1065/1	Type	: Control
Field Name	: dicamba-WATVAL-0001		
Study Number	: T002102-06	Operator	: Kathy White
Sequence File	: T1434.S	Method File	: TNEGDIC.M
		Vial	: 3
Date Acquired	: 13 Oct 2006 13:36	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.30	613.9	100
	185	10.30	401.8	65
	186	0.00	0.0	0

Figure 5 : River water sample fortified with 0.05 µg L^{-1}dicamba. Sample Concentration 25 mL mL^{-1} Recovery = 102%. Target Ion *m/z* = 184



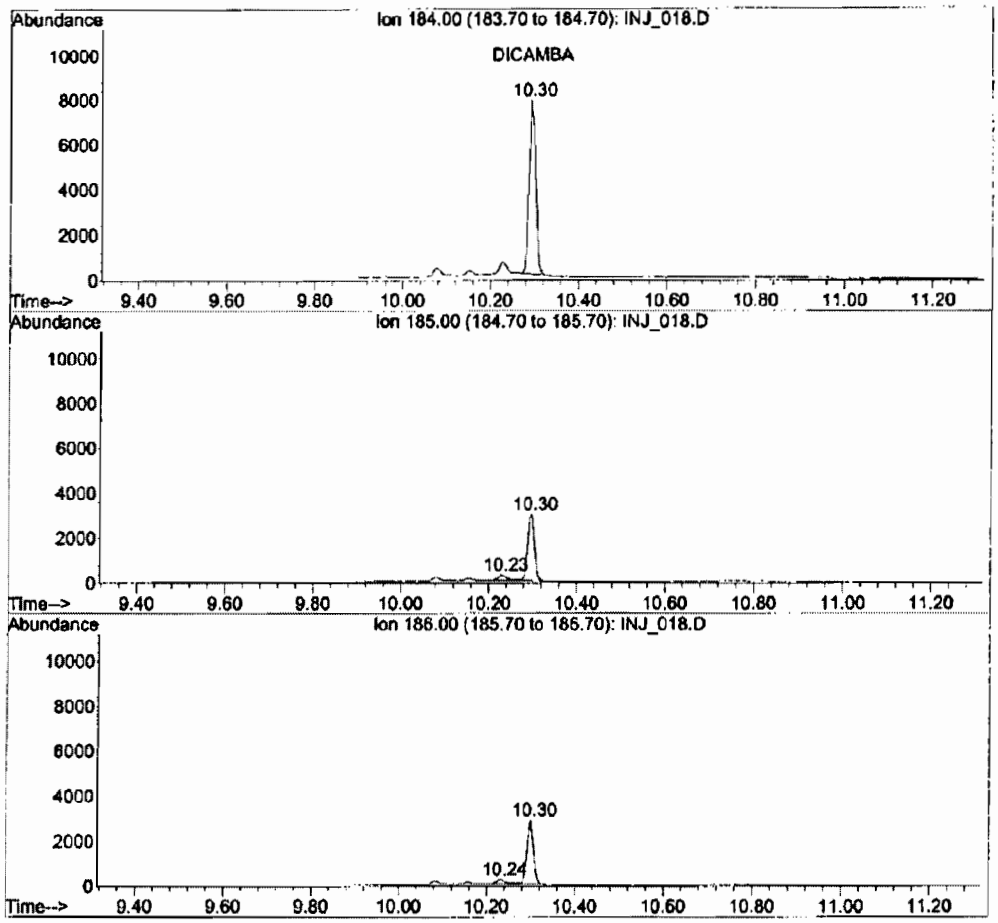
File : C:\MSDCHEM\1\DATA\062017\INJ_009.D
Sample Name : 06-1065/5 Type : Recovery
Field Name : dicamba-WATVAL-0001

Study Number : T002102-06 Operator : Kathy White
Sequence File : T1434.S Method File : TNEGDIC.M
Vial : 7

Date Acquired : 13 Oct 2006 15:52 Matrix Factor : 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.29	8479.1	100
	185	10.30	3350.8	40
	186	10.30	2982.3	35

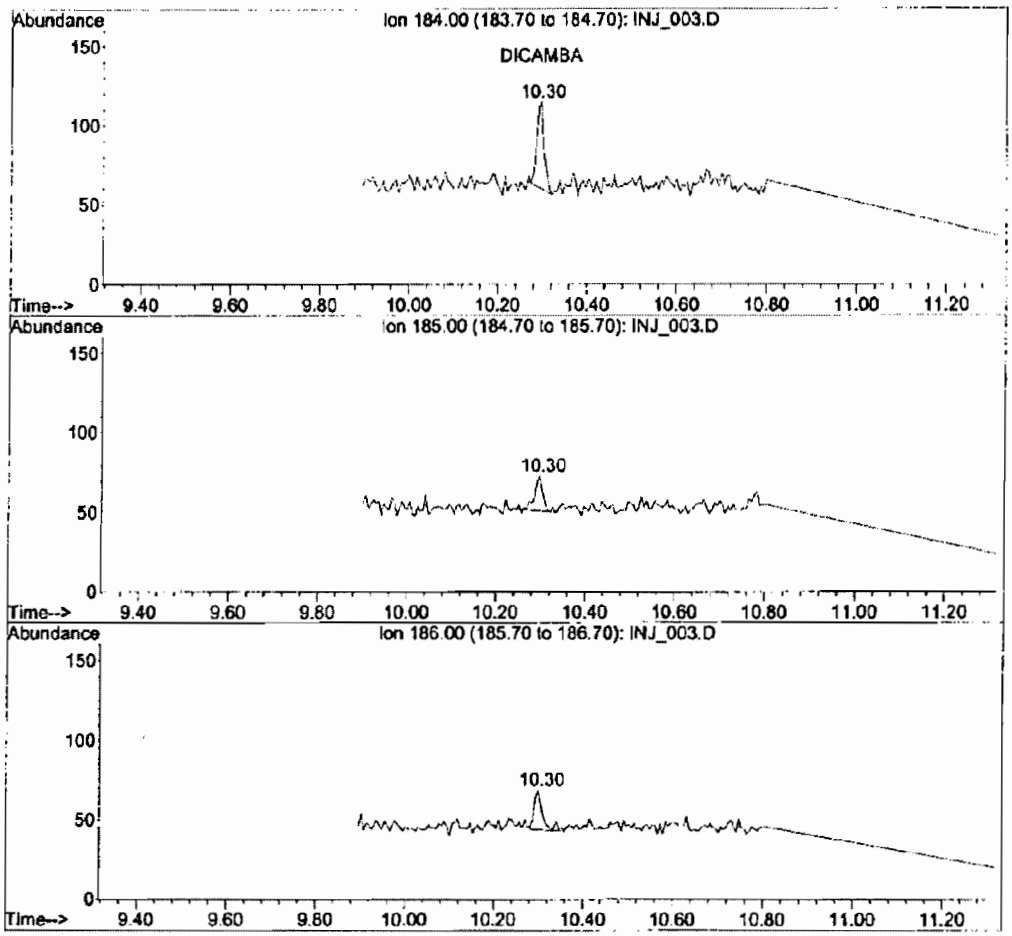
Figure 6 : **River water sample fortified with 0.5 µg L^{-1}dicamba. Sample Concentration 25 mL mL^{-1} Recovery = 101%. Target Ion *m/z* = 184**



File	: C:\MSDCHEM\1\DATA\062017\INJ_018.D				
Sample Name	: 06-1065/10			Type	: Recovery
Field Name	: dicamba-WATVAL-0001				
Study Number	: T002102-06		Operator	: Kathy White	
Sequence File	: T1434.S		Method File	: TNEGDIC.M	
			Vial	: 12	
Date Acquired	: 13 Oct 2006 19:16		Matrix Factor	: 1.00000	

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.30	79568.6	100
	185	10.30	32577.7	41
	186	10.30	28899.7	36

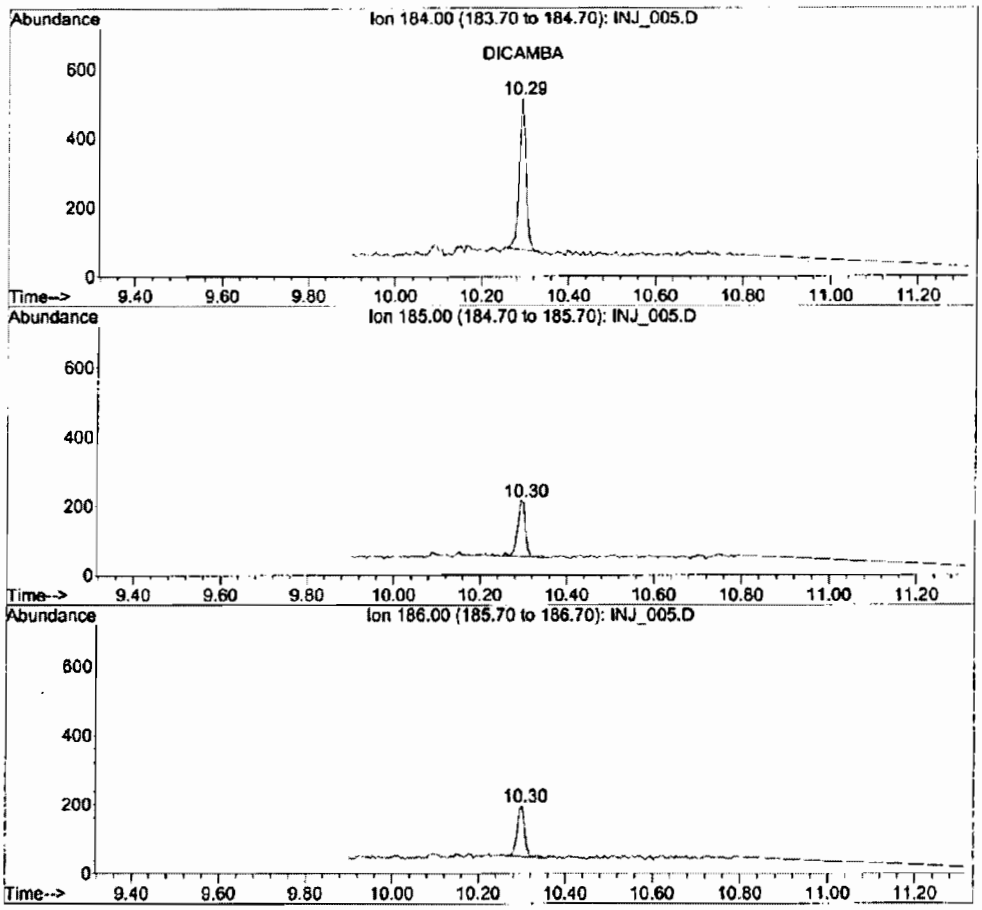
Figure 7 : Ground water: Unfortified sample.
Sample concentration 25 mL mL^{-1}
Residue <LOQ. Target Ion *m/z* = 184



File	: C:\MSDCHEM\1\DATA\062038\INJ_003.D		
Sample Name	: 06-1078/1	Type	: Control
Field Name	: dicamba-WATVAL-0002		
Study Number	: T002102-06	Operator	: Kathy White
Sequence File	: T1438.S	Method File	: TNEGDIC.M
		Vial	: 13
Date Acquired	: 19 Oct 2006 00:46	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.30	622.9	100
	185	10.30	288.7	46
	186	10.30	264.9	43

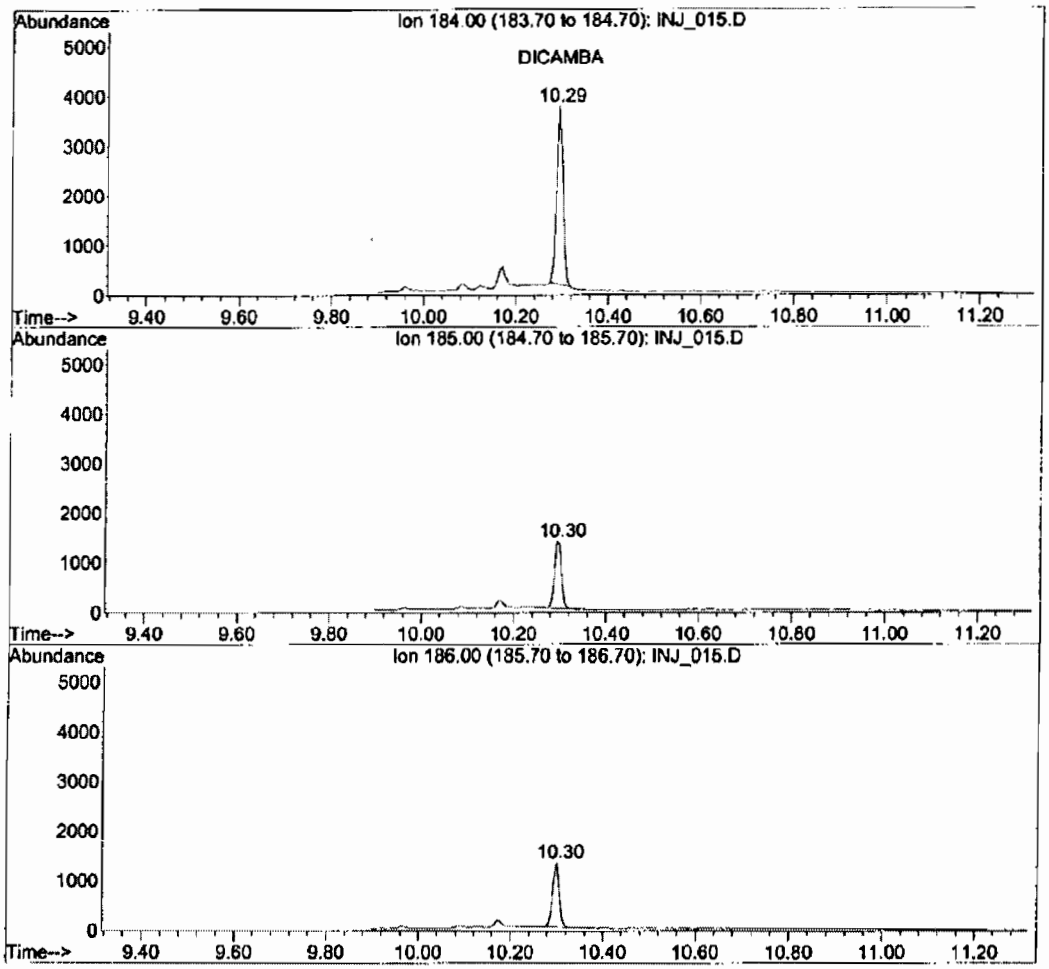
Figure 8 : Ground water sample fortified with 0.05 µg $L^{-1}$with dicamba. Sample concentration 25 mL mL^{-1} Recovery = 105% Target Ion *m/z* = 184



File	: C:\MSDCHEM\1\DATA\062038\INJ_005.D				
Sample Name	: 06-1078/3			Type	: Recovery
Field Name	: dicamba-WATVAL-0002				
Study Number	: T002102-06		Operator	: Kathy White	
Sequence File	: T1438.S		Method File	: TNEGDIC.M	
			Vial	: 15	
Date Acquired	: 19 Oct 2006 1:32		Matrix Factor	: 1.00000	

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.29	4698.6	100
	185	10.30	1932.8	41
	186	10.30	1770.0	38

Figure 9 : **Ground water sample fortified with 0.5 µg $L^{-1}$with dicamba. Sample concentration 25 mL mL^{-1} Recovery = 78% Target Ion *m/z* = 184**



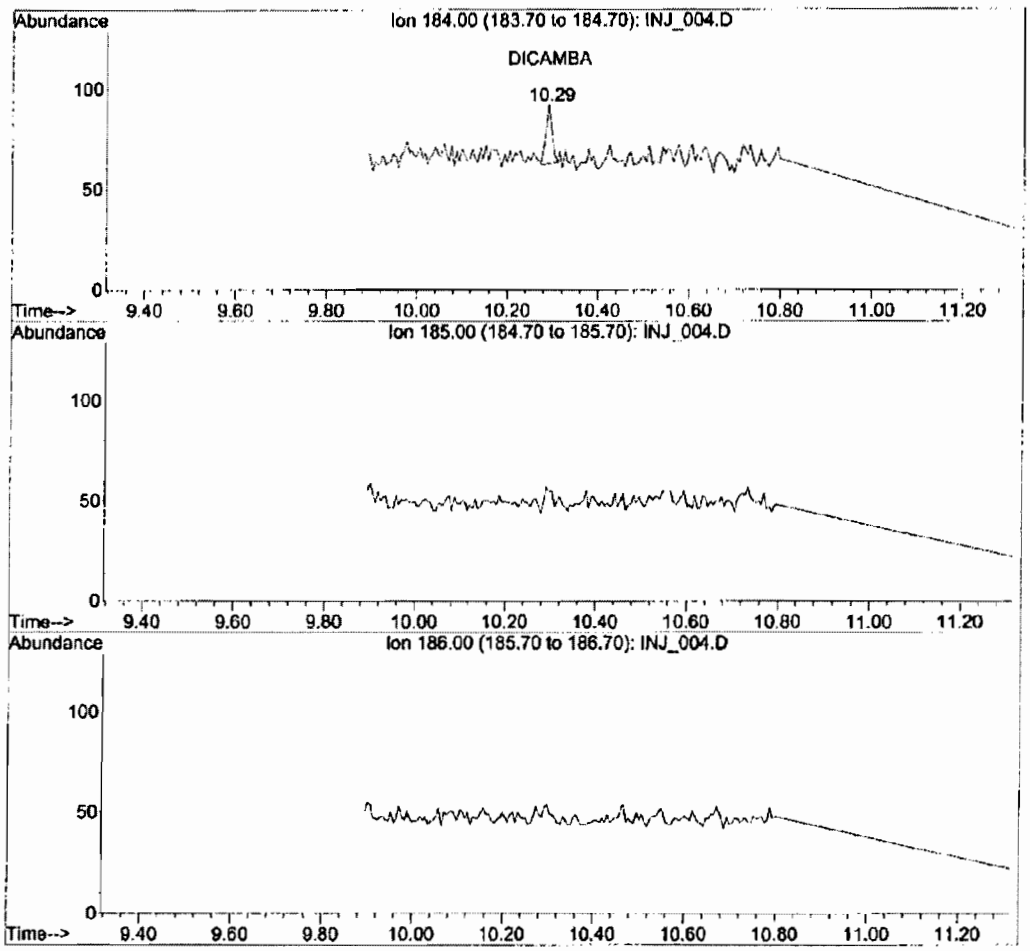
File : C:\MSDCHEM\1\DATA\062038\INJ_015.D
Sample Name : 06-1078/9 Type : Recovery
Field Name : dicamba-WATVAL-0002

Study Number : T002102-06 Operator : Kathy White
Sequence File : T1438.S Method File : TNEGDIC.M
Vial : 21

Date Acquired : 19 Oct 2006 5:19 Matrix Factor : 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.29	32553.0	100
	185	10.30	13994.1	43
	186	10.30	12651.9	39

Figure 10 : Drinking water water: Unfortified sample.
Sample concentration 25 mL mL^{-1}
Residue <LOQ Target Ion *m/z* = 184



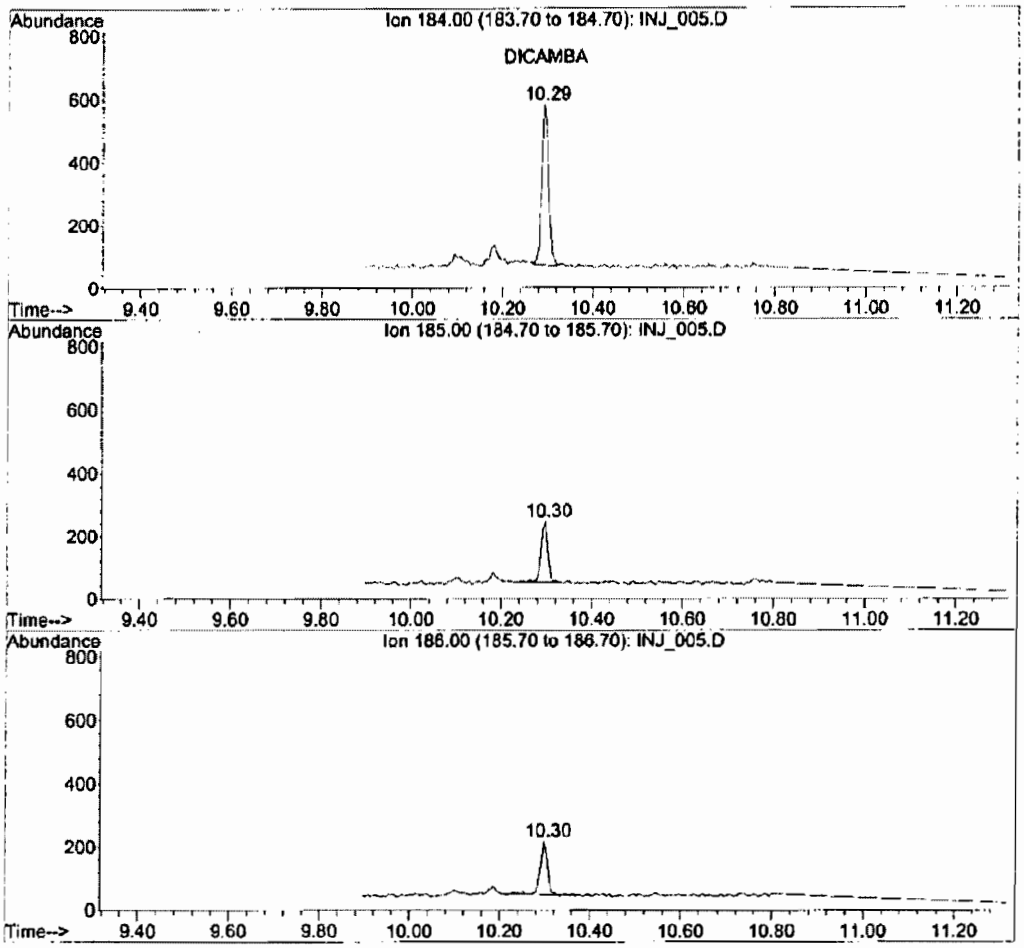
File : C:\MSDCHEM\1\DATA\062043\INJ_004.D
Sample Name : 06-1083/2 Type : Control
Field Name : dicamba-WATVAL-0003

Study Number : T002102-06 Operator : Katherine White
Sequence File : T1439.S Method File : TNEGDIC.M
Vial : 4

Date Acquired : 19 Oct 2006 19:45 Matrix Factor : 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.29	270.8	100
	185	0.00	0.0	0
	186	0.00	0.0	0

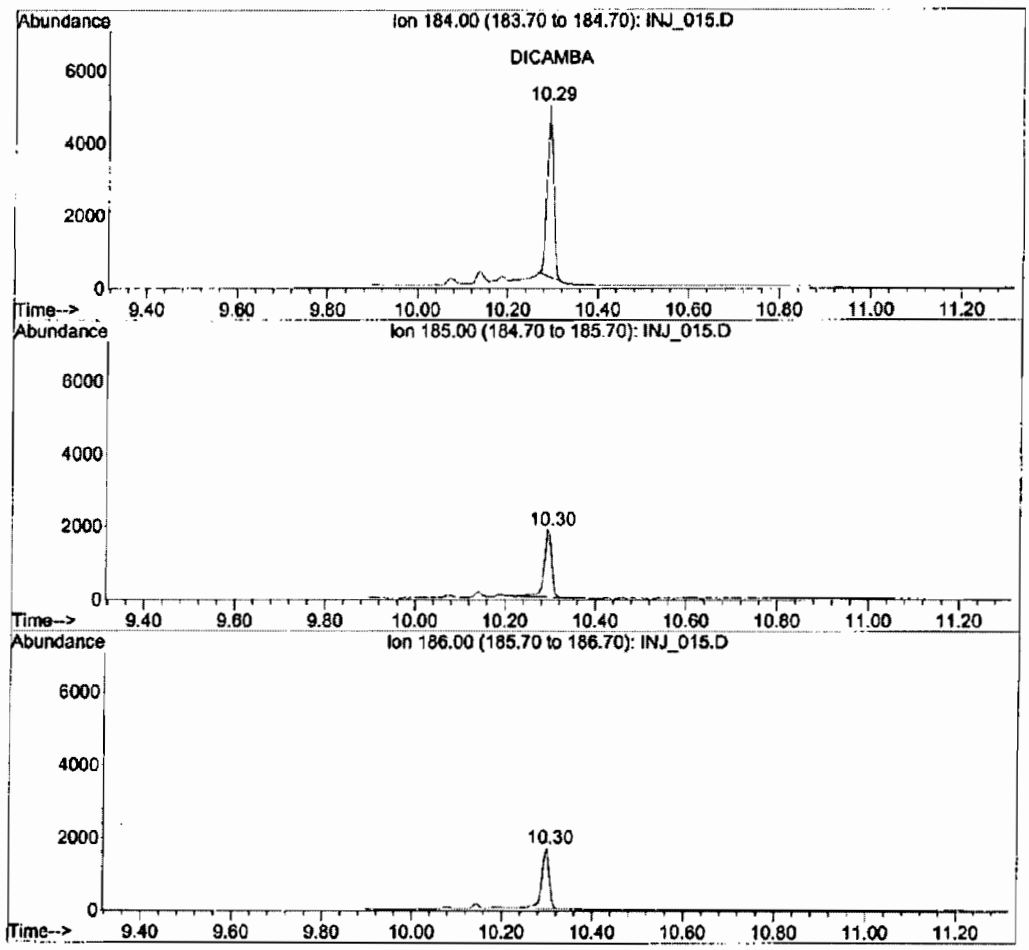
Figure 11 : Drinking water sample fortified with 0.05 µg L^{-1} dicamba. Sample concentration 25 mL mL^{-1}. Recovery = 94%. Target ion *m/z* = 184



File	: C:\MSDCHEM\1\DATA\062043\INJ_005.D				
Sample Name	: 06-1083/3			Type	: Recovery
Field Name	: dicamba-WATVAL-0003				
Study Number	: T002102-06		Operator	: Katherine White	
Sequence File	: T1439.S		Method File	: TNEGDIC.M	
			Vial	: 5	
Date Acquired	: 19 Oct 2006 20:08		Matrix Factor	: 1.00000	

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.29	5224.4	100
	185	10.30	1953.6	37
	186	10.30	1840.3	35

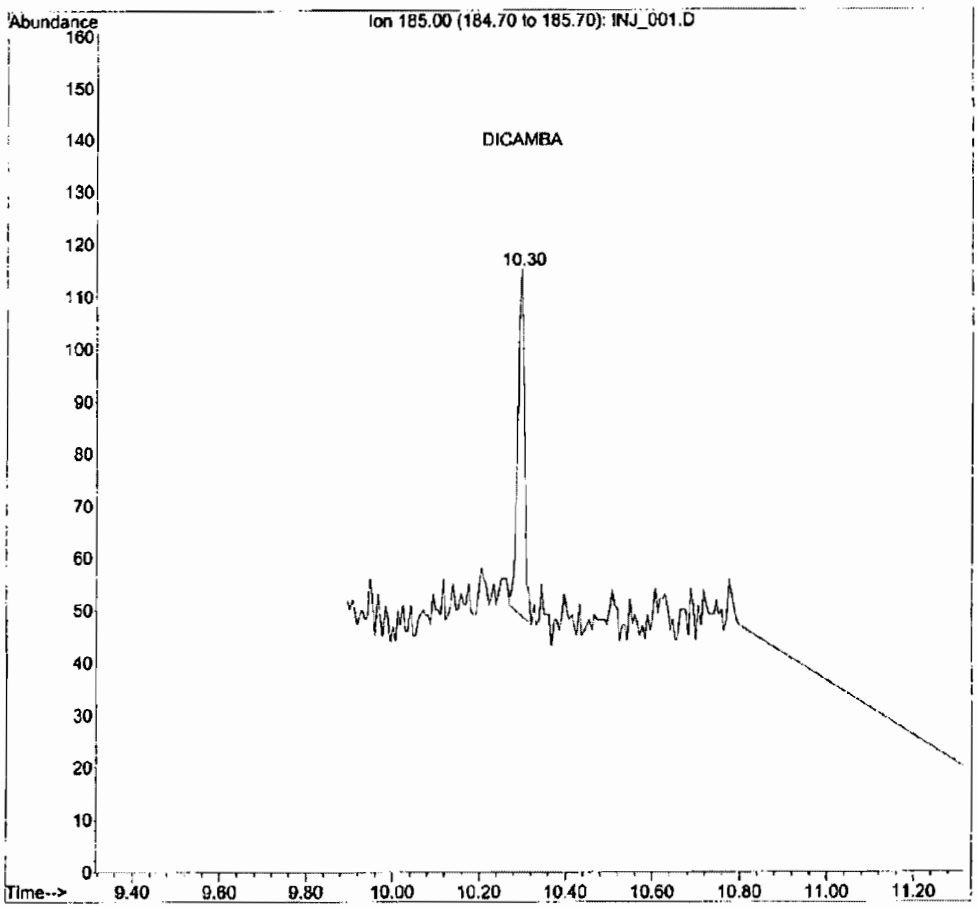
Figure 12 : Drinking water sample fortified with 0.5 µg L^{-1} dicamba. Sample concentration 25 mL mL^{-1}. Recovery = 88%. Target ion *m/z* = 184



File	: C:\MSDCHEM\1\DATA\062043\INJ_015.D				
Sample Name	: 06-1083/9			Type	: Recovery
Field Name	: dicamba-WATVAL-0003				
Study Number	: T002102-06		Operator	: Katherine White	
Sequence File	: T1439.S		Method File	: TNEGDIC.M	
			Vial	: 11	
Date Acquired	: 19 Oct 2006 23:56		Matrix Factor	: 1.00000	

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	184	10.29	45947.9	100
	185	10.30	20817.6	45
	186	10.30	18540.8	40

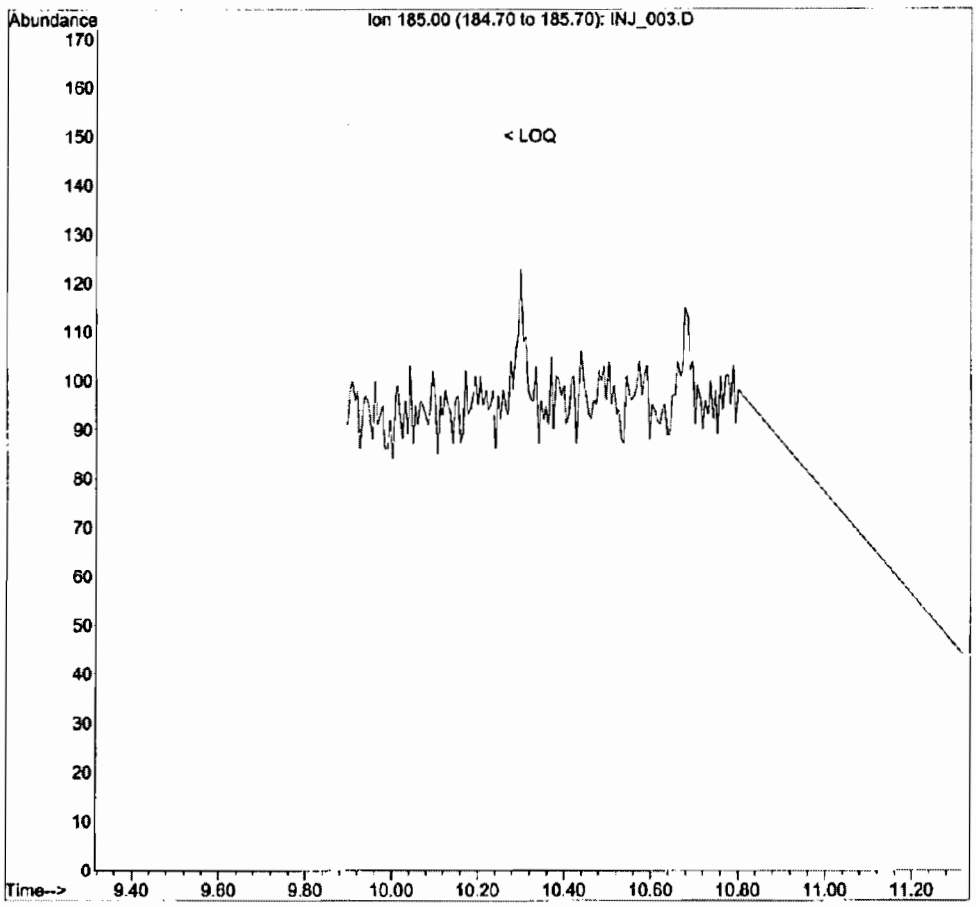
Figure 13 : 0.5 μg mL^{-1} Dicamba Standard.
Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062043\INJ_001.D		
Sample Name	: 06-2043/1	Type	: Standard
Field Name	:		
Study Number	: T002102-06	Operator	: Katherine White
Sequence File	: T1439.S	Method File	: TNEGDIC_2.M
		Vial	: 1
Date Acquired	: 19 Oct 2006 18:37	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	185	10.30	743.1	100

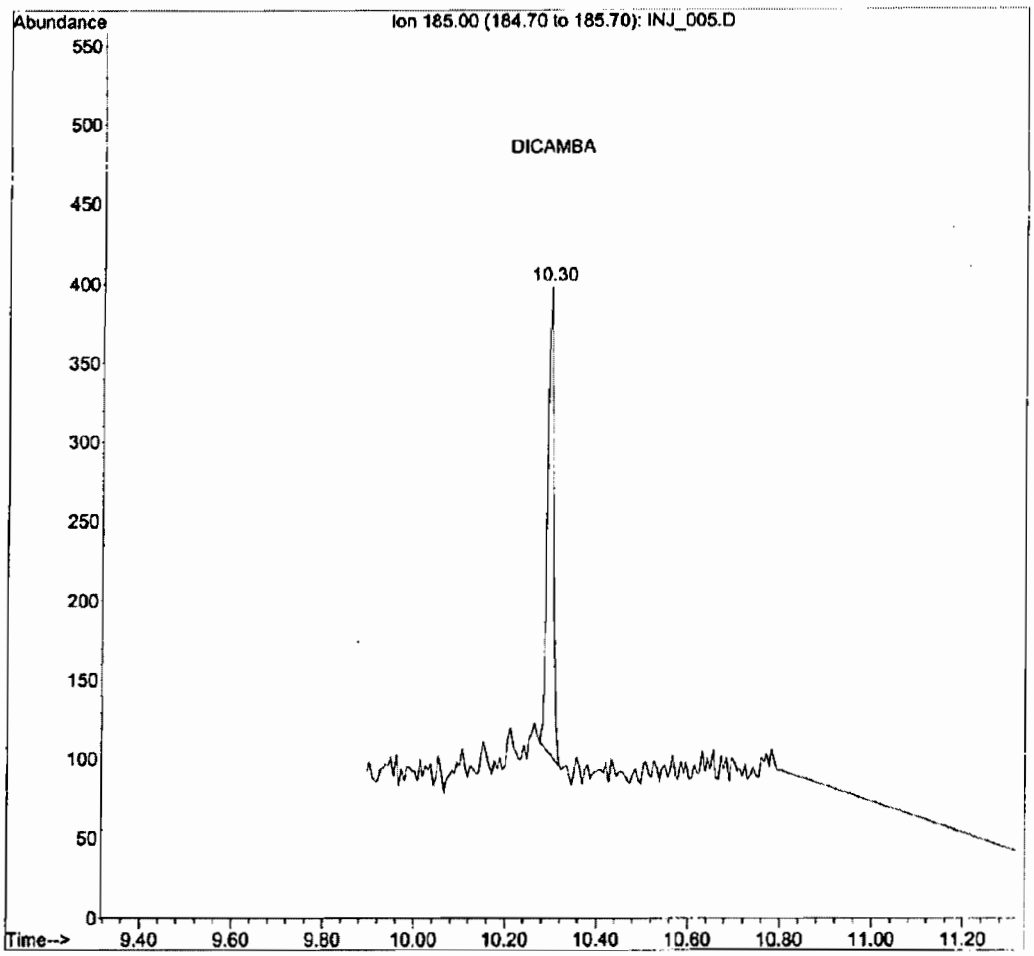
Figure 14 : River water : Unfortified.
Sample concentration 25 mL mL^{-1}.
Residue <LOQ Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062017\INJ_003.D		
Sample Name	: 06-1065/1	Type	: Control
Field Name	: dicamba-WATVAL-0001		
Study Number	: T002102-06	Operator	: Kathy White
Sequence File	: T1434.S	Method File	: TNEGDIC_2.M
		Vial	: 3
Date Acquired	: 13 Oct 2006 13:36	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
Not Detected				

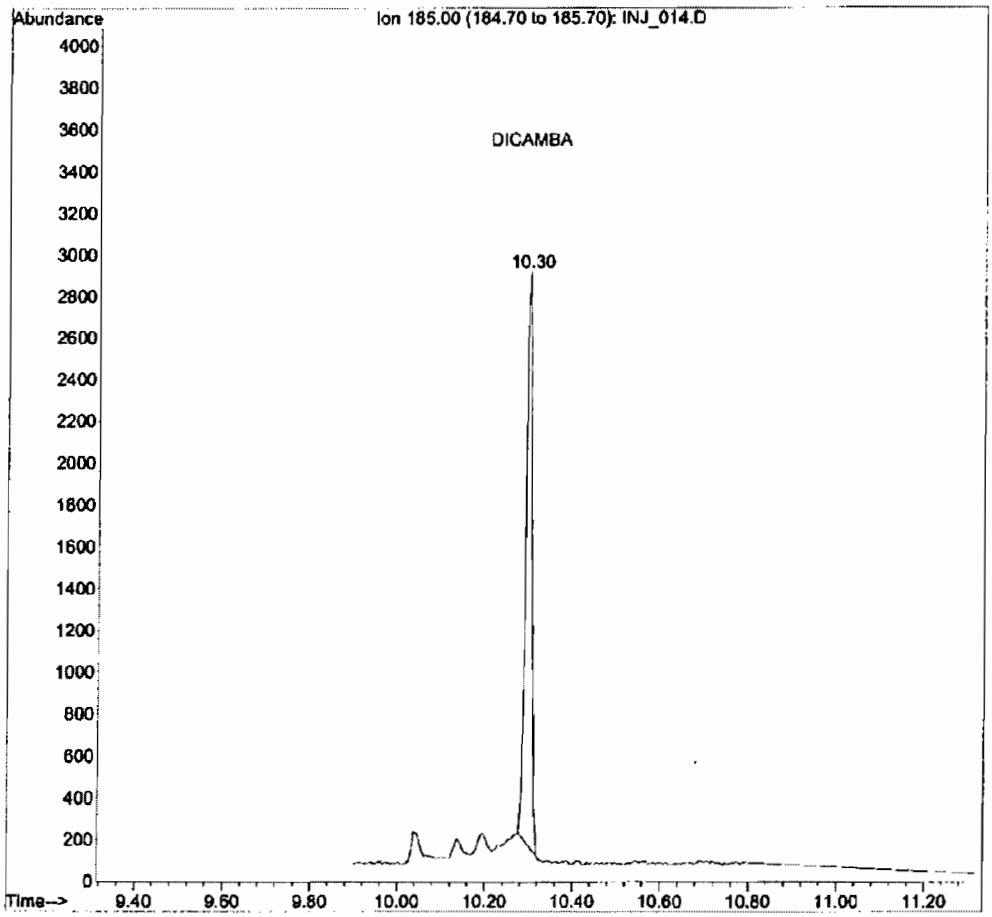
Figure 15 : River water sample fortified with 0.05 µg L^{-1}dicamba. Sample Concentration 25 mL mL^{-1} Recovery = 85%. Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062017\INJ_005.D		
Sample Name	: 06-1065/3	Type	: Recovery
Field Name	: dicamba-WATVAL-0001		
Study Number	: T002102-06	Operator	: Kathy White
Sequence File	: T1434.S	Method File	: TNEGDIC_2.M
		Vial	: 5
Date Acquired	: 13 Oct 2006 14:22	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	185	10.30	2838.5	100

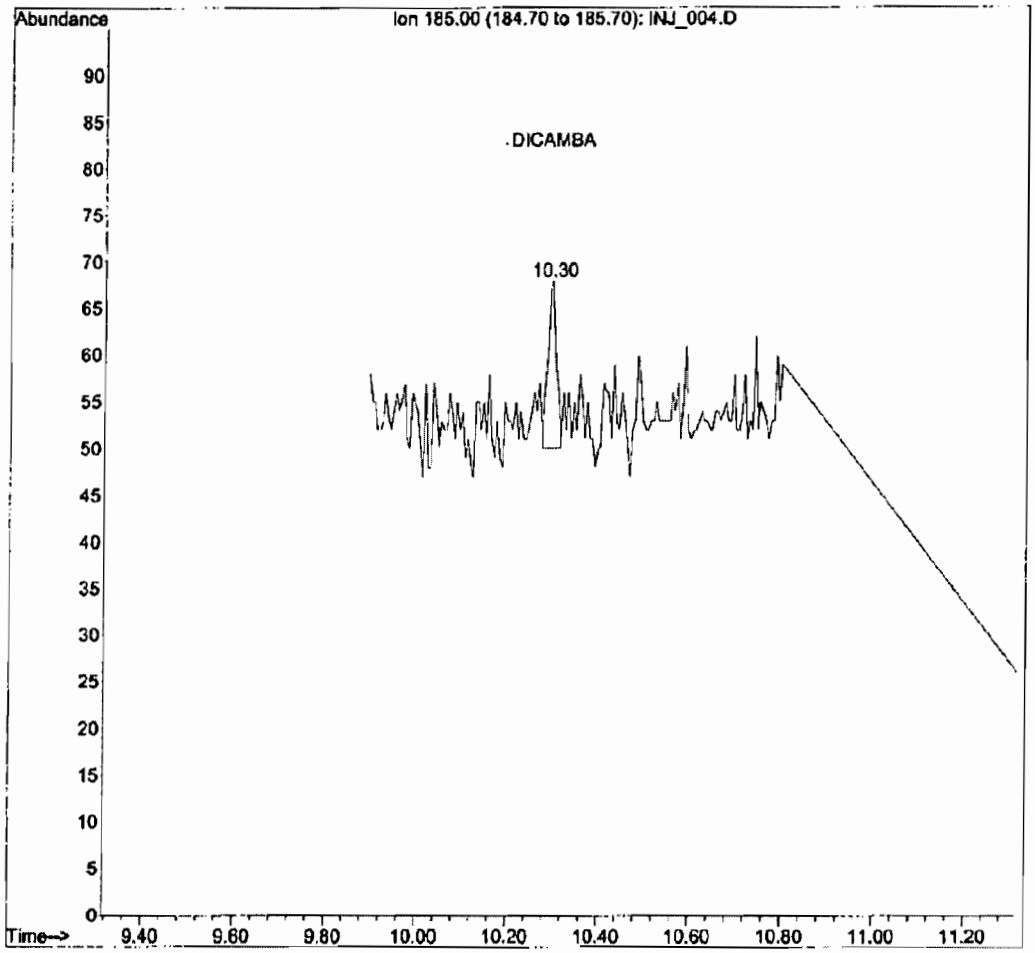
Figure 16 : River water sample fortified with 0.5 µg L^{-1}dicamba. Sample Concentration 25 mL mL^{-1} Recovery = 83%. Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062017\INJ_014.D		
Sample Name	: 06-1065/8	Type	: Recovery
Field Name	: dicamba-WATVAL-0001		
Study Number	: T002102-06	Operator	: Kathy White
Sequence File	: T1434.S	Method File	: TNEGDIC_2.M
		Vial	: 10
Date Acquired	: 13 Oct 2006 17:45	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	185	10.30	27249.6	100

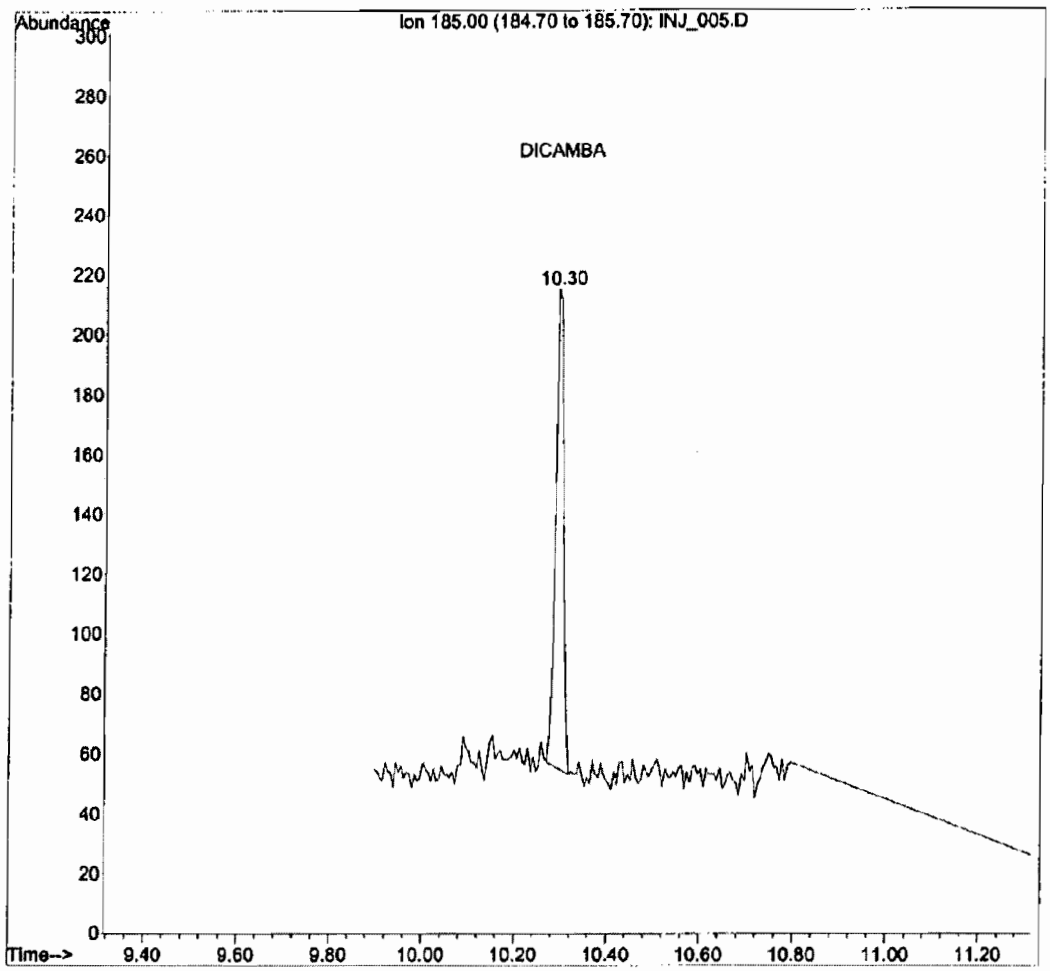
Figure 17 : Ground water: Unfortified sample.
Sample concentration 25 mL mL^{-1}
Residue <LOQ Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062038\INJ_004.D		
Sample Name	: 06-1078/2	Type	: Control
Field Name	: dicamba-WATVAL-0002		
Study Number	: T002102-06	Operator	: Kathy White
Sequence File	: T1438.S	Method File	: TNEGDIC_2.M
		Vial	: 14
Date Acquired	: 19 Oct 2006 1:09	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	185	10.30	246.5	100

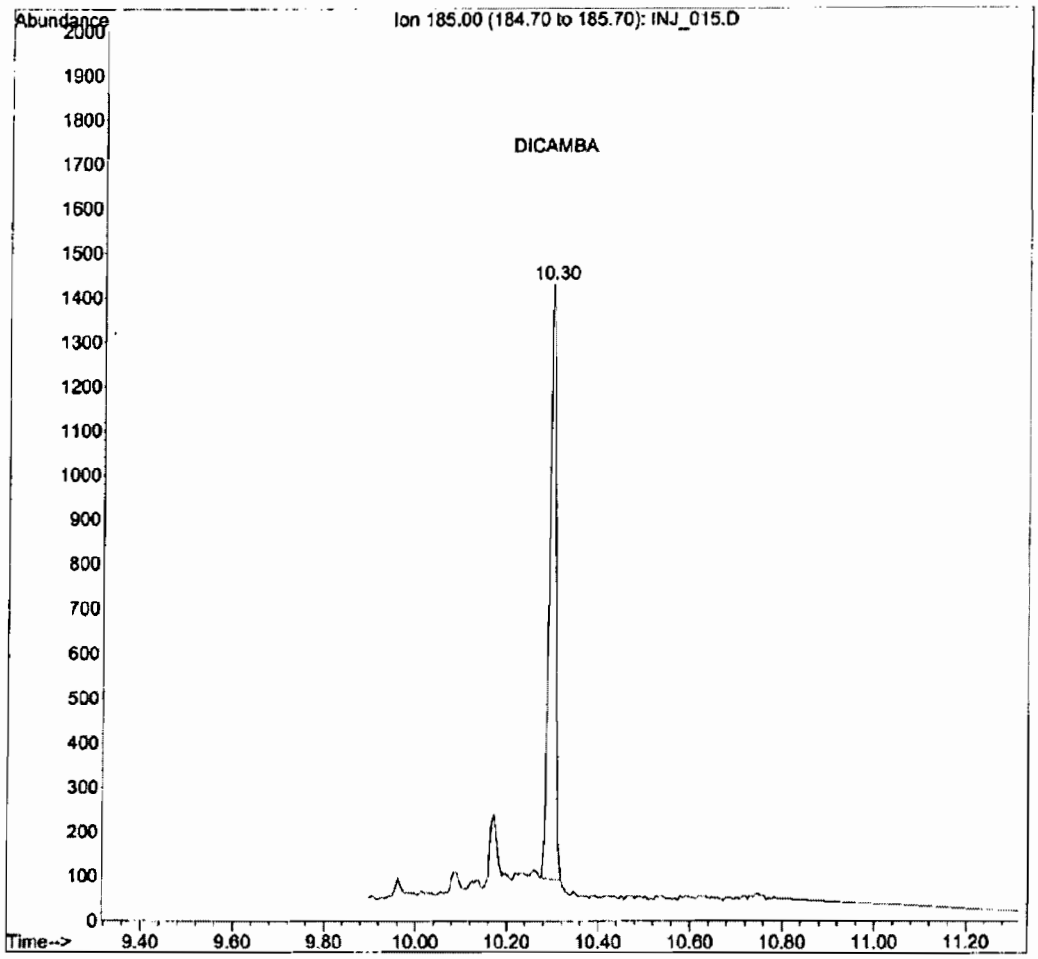
Figure 18 : Ground water sample fortified with 0.05 µg $L^{-1}$with dicamba. Sample concentration 25 mL mL^{-1} Recovery = 105% Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062038\INJ_005.D		
Sample Name	: 06-1078/3	Type	: Recovery
Field Name	: dicamba-WATVAL-0002		
Study Number	: T002102-06	Operator	: Kathy White
Sequence File	: T1438.S	Method File	: TNEGDIC_2.M
		Vial	: 15
Date Acquired	: 19 Oct 2006 1:32	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	185	10.30	1916.6	100

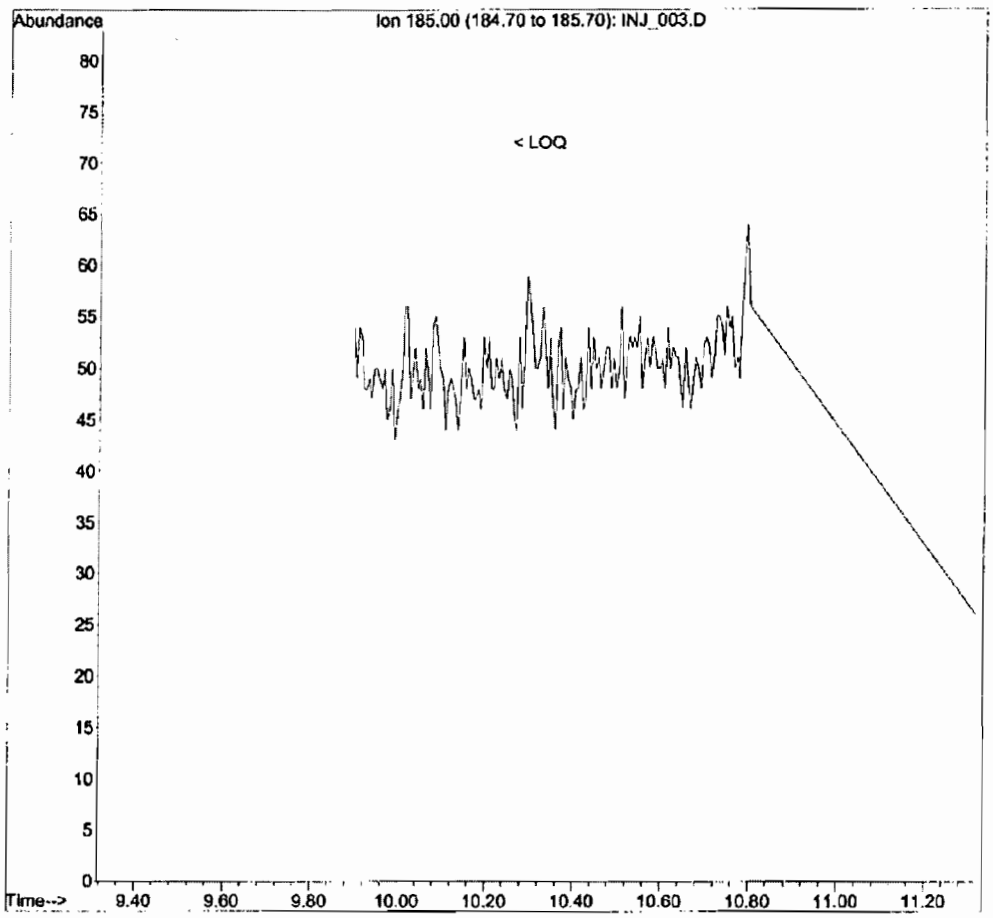
Figure 19 : Ground water sample fortified with 0.5 µg L^{-1} with dicamba. Sample concentration 25 mL mL^{-1} Recovery = 78% Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062038\INJ_015.D		
Sample Name	: 06-1078/9	Type	: Recovery
Field Name	: dicamba-WATVAL-0002		
Study Number	: T002102-06	Operator	: Kathy White
Sequence File	: T1438.S	Method File	: TNEGDIC_2.M
		Vial	: 21
Date Acquired	: 19 Oct 2006 5:19	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	185	10.30	13435.5	100

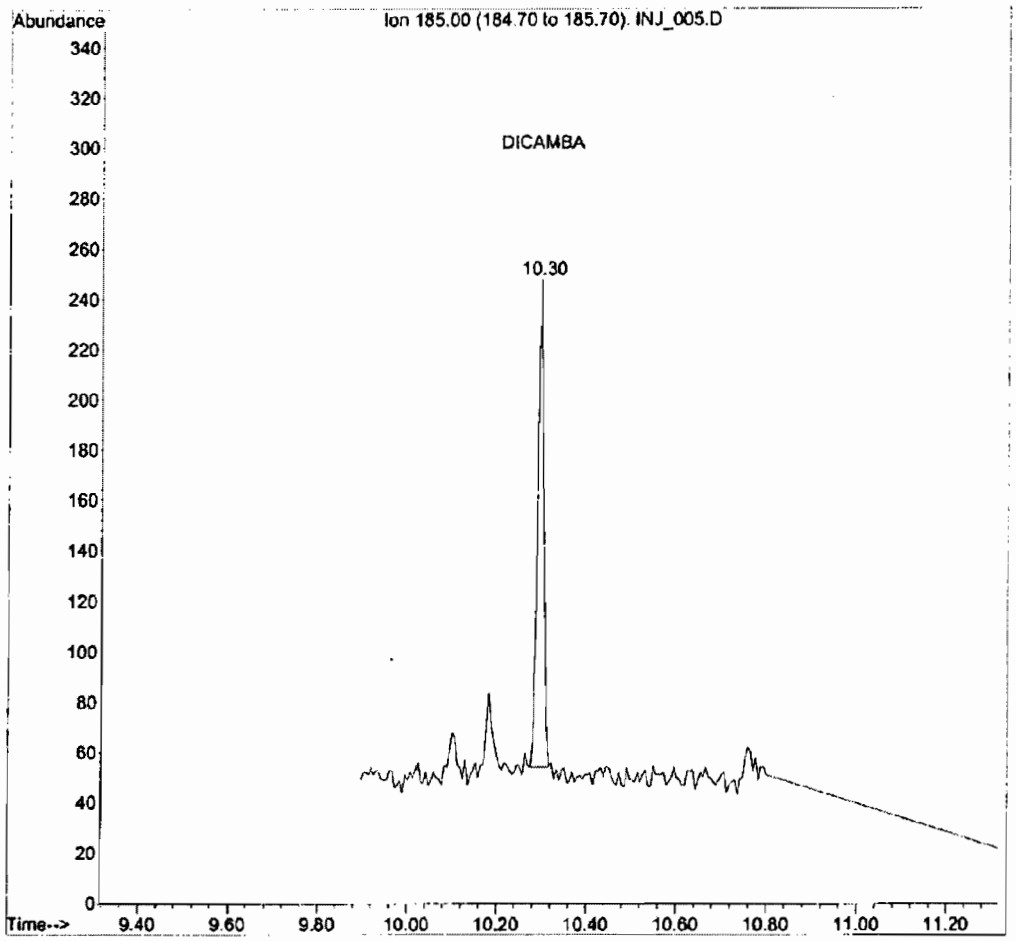
Figure 20 : Drinking water: Unfortified sample.
Sample concentration 25 mL mL^{-1}
Residue <LOQ Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062043\INJ_003.D		
Sample Name	: 06-1083/1	Type	: Control
Field Name	: dicamba-WATVAL-0003		
Study Number	: T002102-06	Operator	: Katherine White
Sequence File	: T1439.S	Method File	: TNEGDIC_2.M
		Vial	: 3
Date Acquired	: 19 Oct 2006 19:23	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
Not Detected				

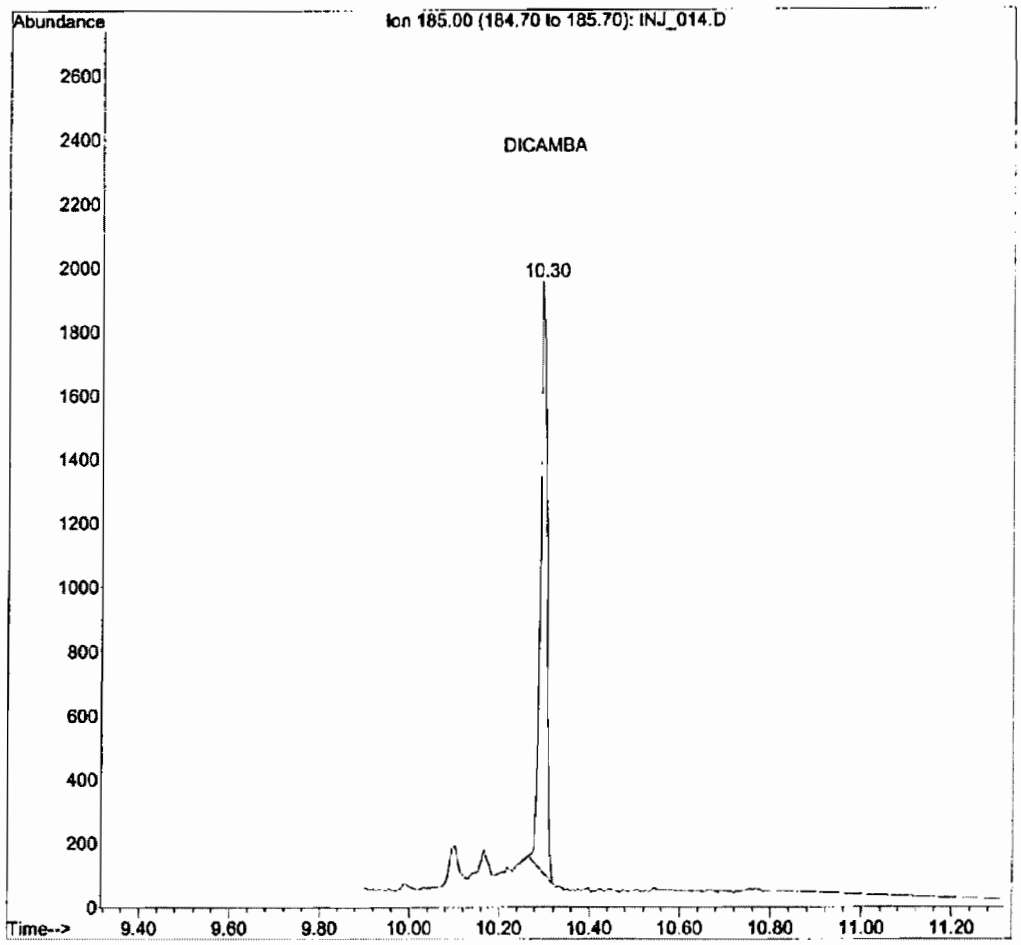
Figure 21 : Drinking water sample fortified with 0.05 µg L^{-1} dicamba. Sample concentration 25 mL mL^{-1}. Recovery = 79% Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062043\INJ_005.D				
Sample Name	: 06-1083/3			Type	: Recovery
Field Name	: dicamba-WATVAL-0003				
Study Number	: T002102-06		Operator	: Katherine White	
Sequence File	: T1439.S		Method File	: TNEGDIC_2.M	
			Vial	: 5	
Date Acquired	: 19 Oct 2006 20:08		Matrix Factor	: 1.00000	

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	185	10.30	1853.8	100

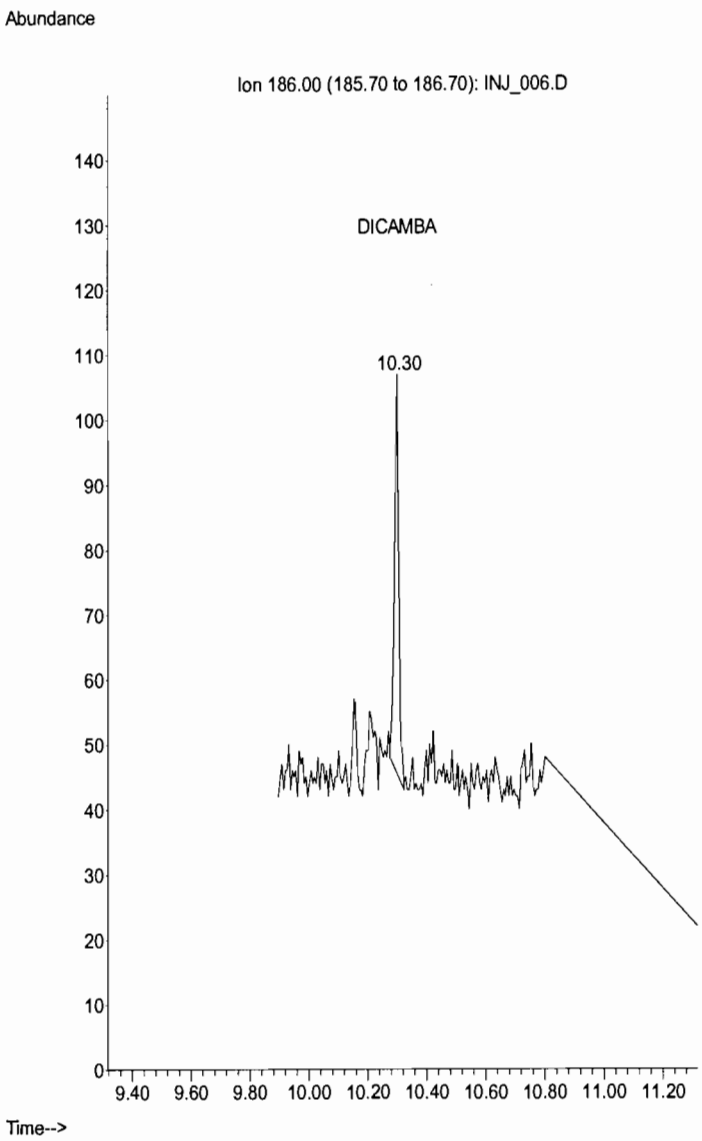
Figure 22 : Drinking water sample fortified with 0.5 µg L^{-1} dicamba. Sample concentration 25 mL mL^{-1}. Recovery = 85% Qualifier Ion *m/z* = 185



File	: C:\MSDCHEM\1\DATA\062043\INJ_014.D		
Sample Name	: 06-1083/8	Type	: Recovery
Field Name	: dicamba-WATVAL-0003		
Study Number	: T002102-06	Operator	: Katherine White
Sequence File	: T1439.S	Method File	: TNEGDIC_2.M
		Vial	: 10
Date Acquired	: 19 Oct 2006 23:33	Matrix Factor	: 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	185	10.30	18696.3	100

Figure 23 : 0.5 µg mL^{-1} Dicamba Standard.
Qualifier Ion *m/z* = 186



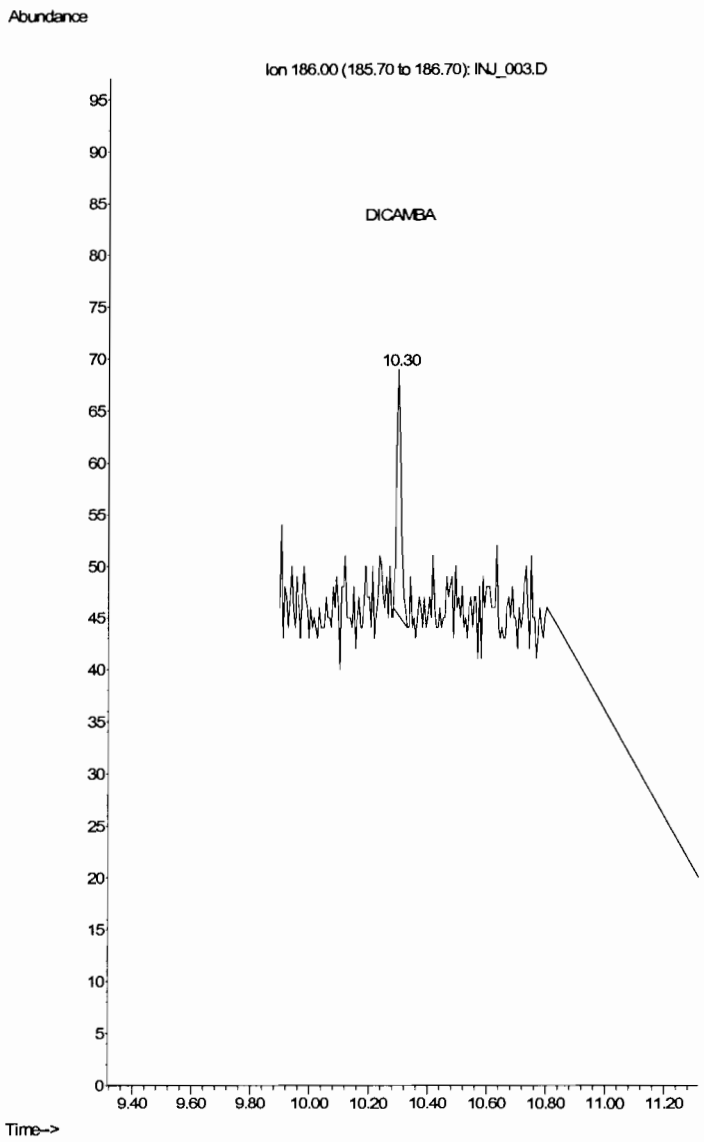
File
Sample Name 06-2038/6 Type Standard
Field Name

Study Number T002102-06 Operator Kathy White
Sequence File T1438.S Method File TNEGDIC_3.M
Vial 11

Date Acquired 19 Oct 2006 1:55 Matrix Factor1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	186	10.30	616.3	100

Figure 24 : Groundwater : Unfortified.
Sample concentration 25 mL mL^{-1}.
Residue <LOQ Qualifier Ion *m/z* = 186



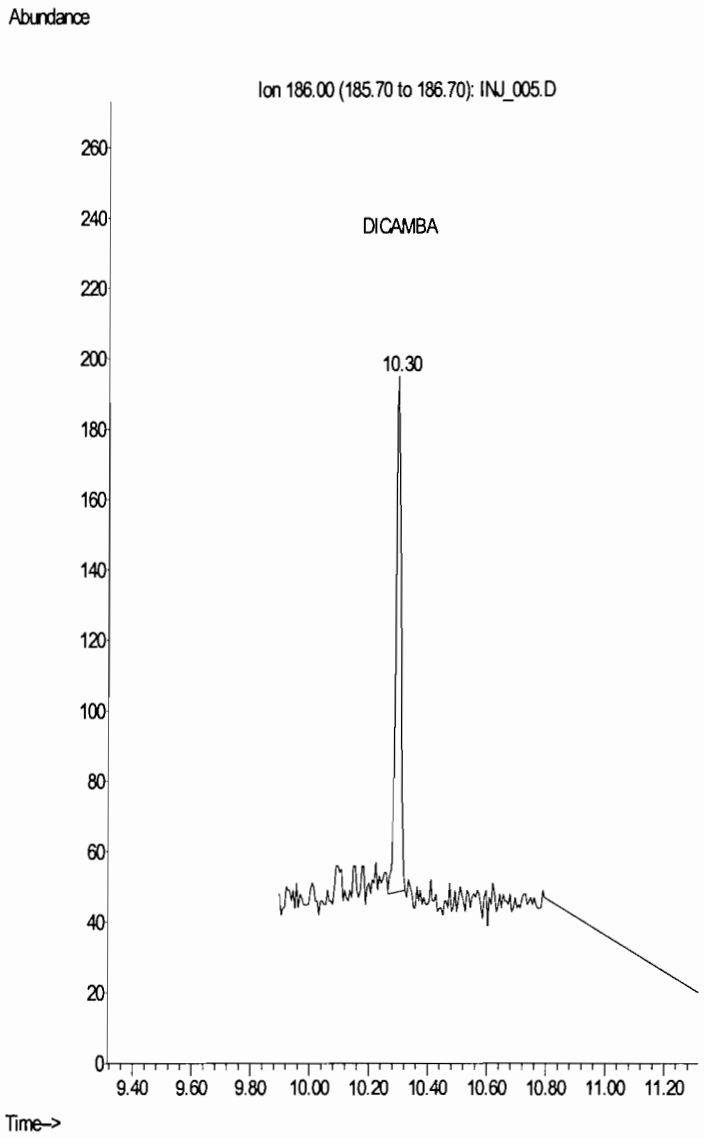
File
Sample Name 06-1078/1 Type Control
Field Name dicamba-WATVAL-0002

Study Number T002102-06 Operator Kathy White
Sequence File T1438.S Method File TNEGDIC_3.M
Vial 13

Date Acquired 19 Oct 2006 00:46 Matrix Factor1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	186	10.30	255.7	100

Figure 25 : Groundwater sample fortified with 0.05 µg L^{-1}dicamba. Sample Concentration 25 mL mL^{-1} Recovery = 104%. Qualifier Ion *m/z* = 186

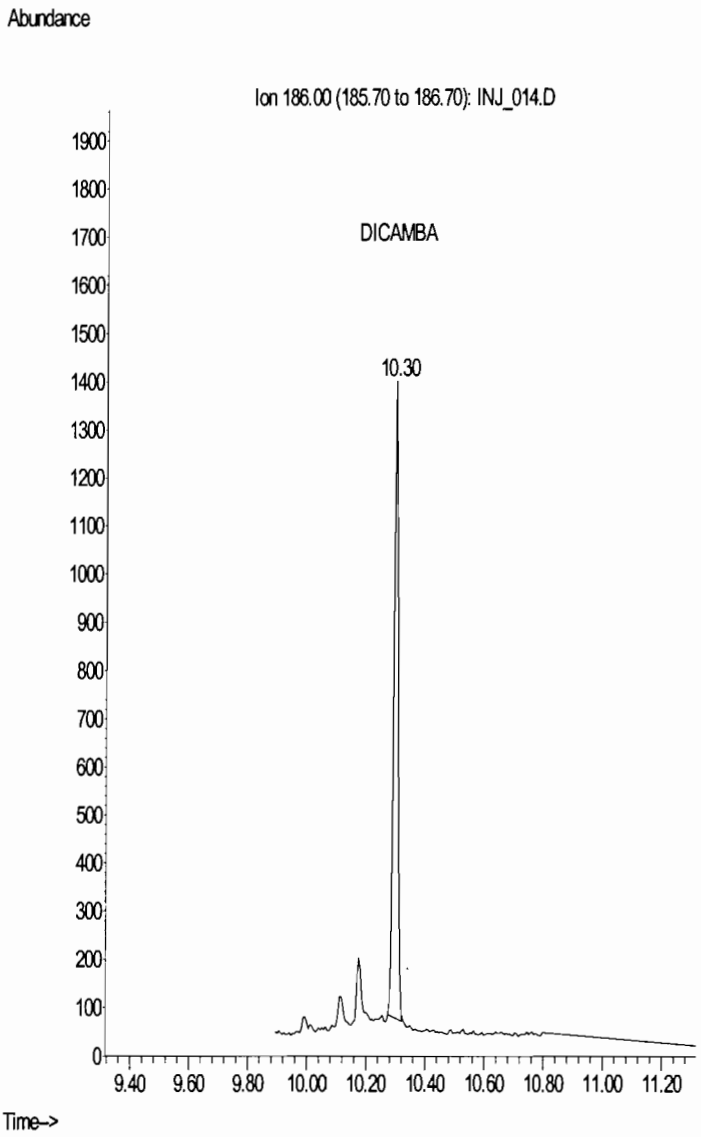


File

Sample Name	06-1078/3		Type	Recovery	
Field Name	dicamba-WATVAL-0002				
Study Number	T002102-06	Operator	Kathy White		
Sequence File	T1438.S	Method File	TNEGDIC_3.M		
		Vial	15		
Date Acquired	19 Oct 2006	1:32	Matrix Factor	1.00000	

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	186	10.30	1769.7	100

Figure 26 : Groundwater sample fortified with 0.5 µg L^{-1}dicamba. Sample Concentration 25 mL mL^{-1} Recovery = 81%. Qualifier Ion *m/z* = 186



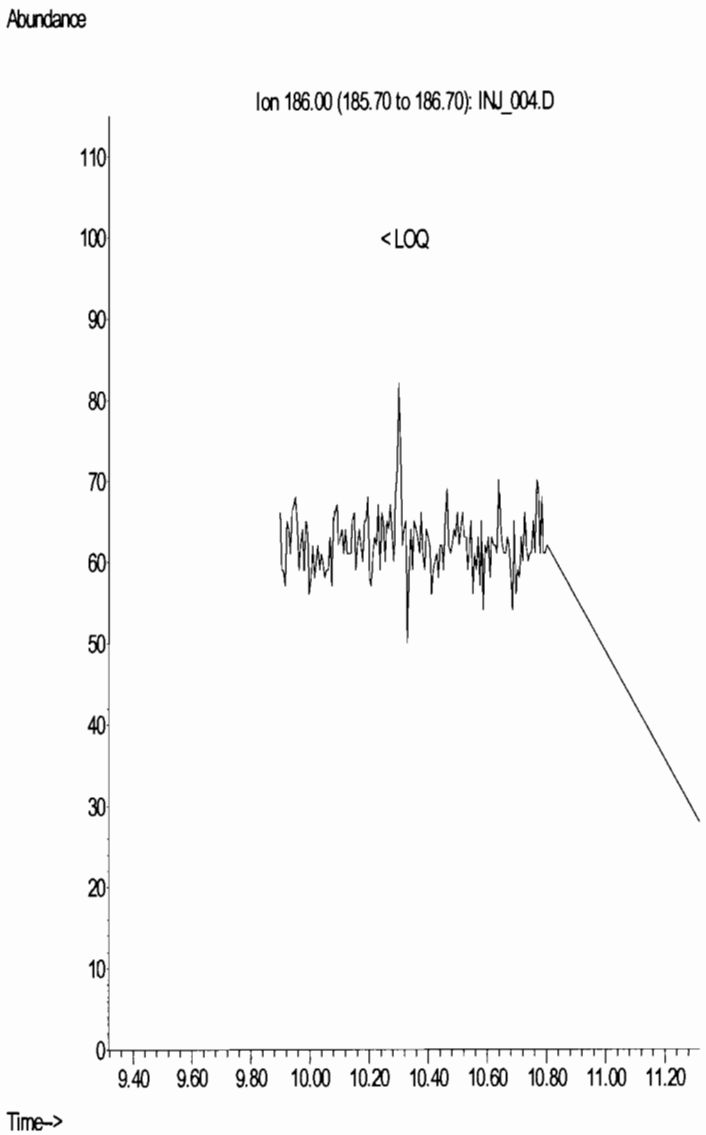
File
Sample Name 06-1078/8 Type Recovery
Field Name dicamba-WATVAL-0002

Study Number T002102-06 Operator Kathy White
Sequence File T1438.S Method File TNEGDIC_3.M
Vial 20

Date Acquired 19 Oct 2006 4:57 Matrix Factor1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	186	10.30	13710.8	100

Figure 27 : River water: Unfortified sample.
Sample concentration 25 mL mL^{-1}
Residue <LOQ Qualifier Ion *m/z* = 186



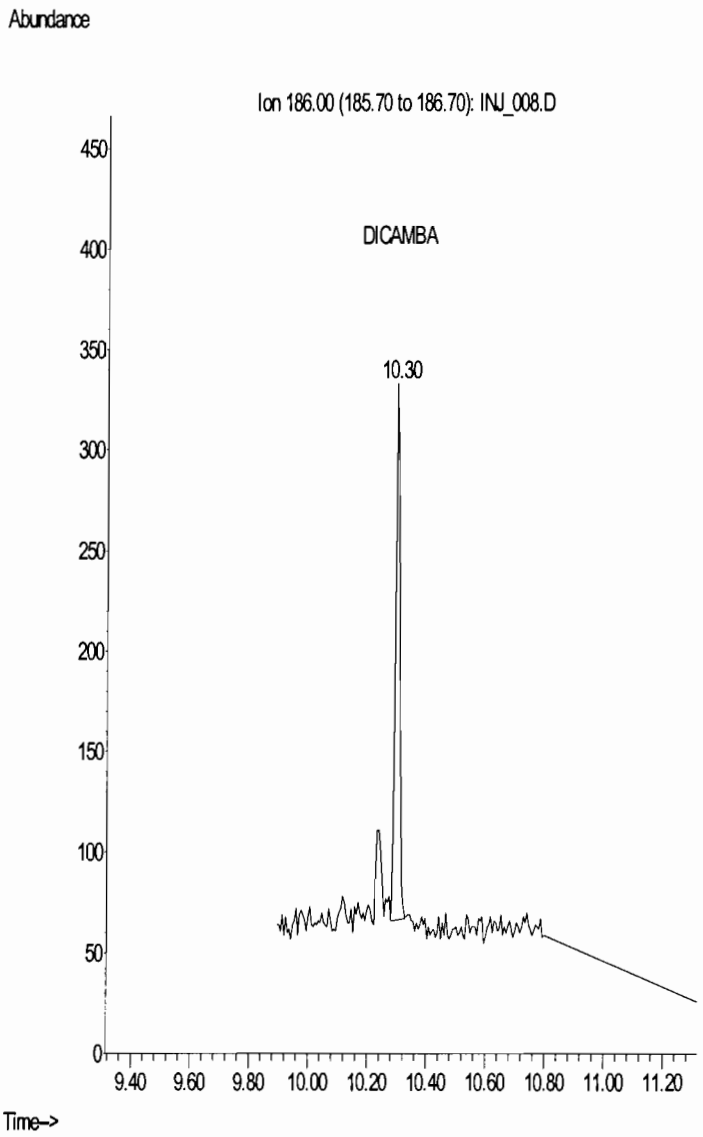
File
Sample Name 06-1065/2 Type Control
Field Name dicamba-WATVAL-0001

Study Number T002102-06 Operator Kathy White
Sequence File T1434.S Method File TNEGDIC_3.M
Vial 4

Date Acquired 13 Oct 2006 13:59 Matrix Factor 1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
	Not Detected			

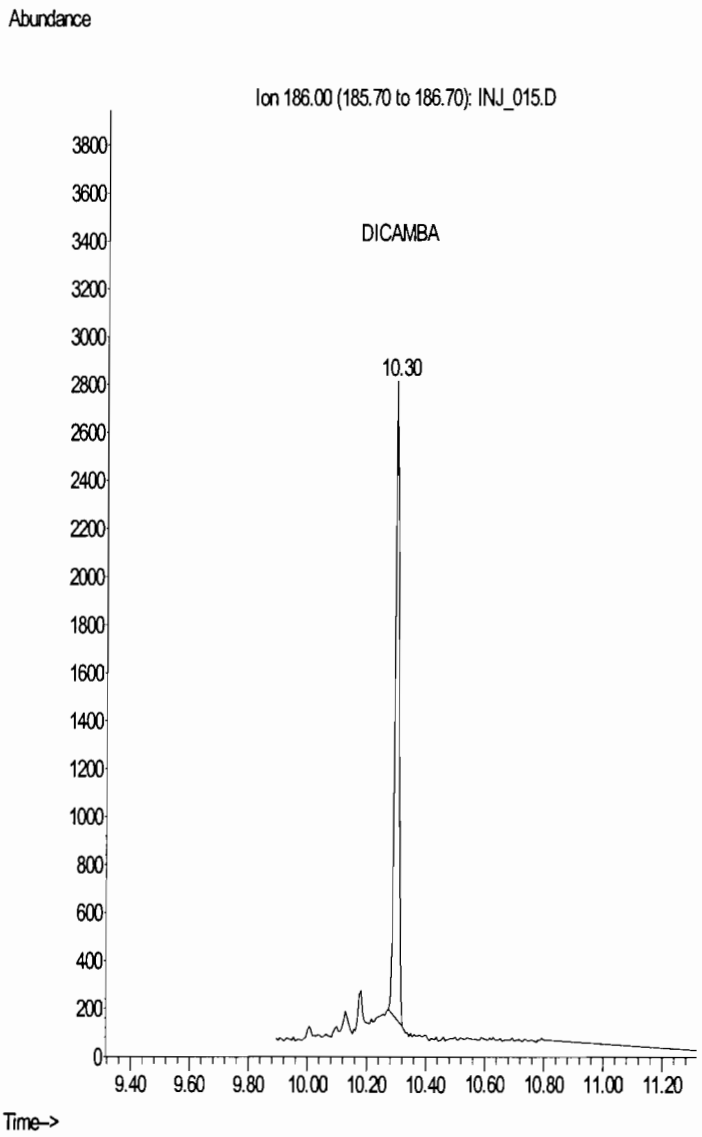
Figure 28 : River water sample fortified with 0.05 µg L^{-1} with dicamba. Sample concentration 25 mL mL^{-1} Recovery = 84% Qualifier Ion *m/z* = 186



File					
Sample Name	06-1065/4			Type	Recovery
Field Name	dicamba-WATVAL-0001				
Study Number	T002102-06		Operator	Kathy White	
Sequence File	T1434.S		Method File	TNEGDIC_3.M	
			Vial	6	
Date Acquired	13 Oct 2006		15:30	Matrix Factor	1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	186	10.30	2716.1	100

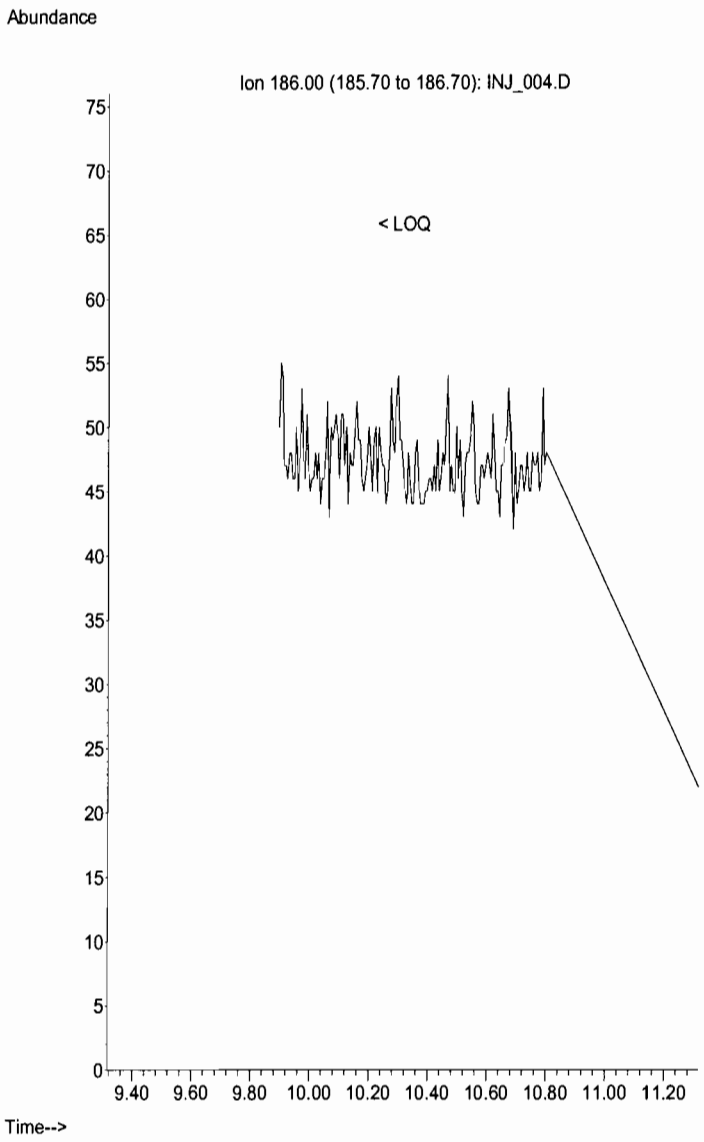
Figure 29 : River water sample fortified with 0.5 µg $L^{-1}$with dicamba. Sample concentration 25 mL mL^{-1} Recovery = 84% Qualifier Ion *m/z* = 186



File					
Sample Name	06-1065/9			Type	Recovery
Field Name	dicamba-WATVAL-0001				
Study Number	T002102-06		Operator	Kathy White	
Sequence File	T1434.S		Method File	TNEGDIC_3.M	
			Vial	11	
Date Acquired	13 Oct 2006		18:08	Matrix Factor	1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	186	10.30	25831.9	100

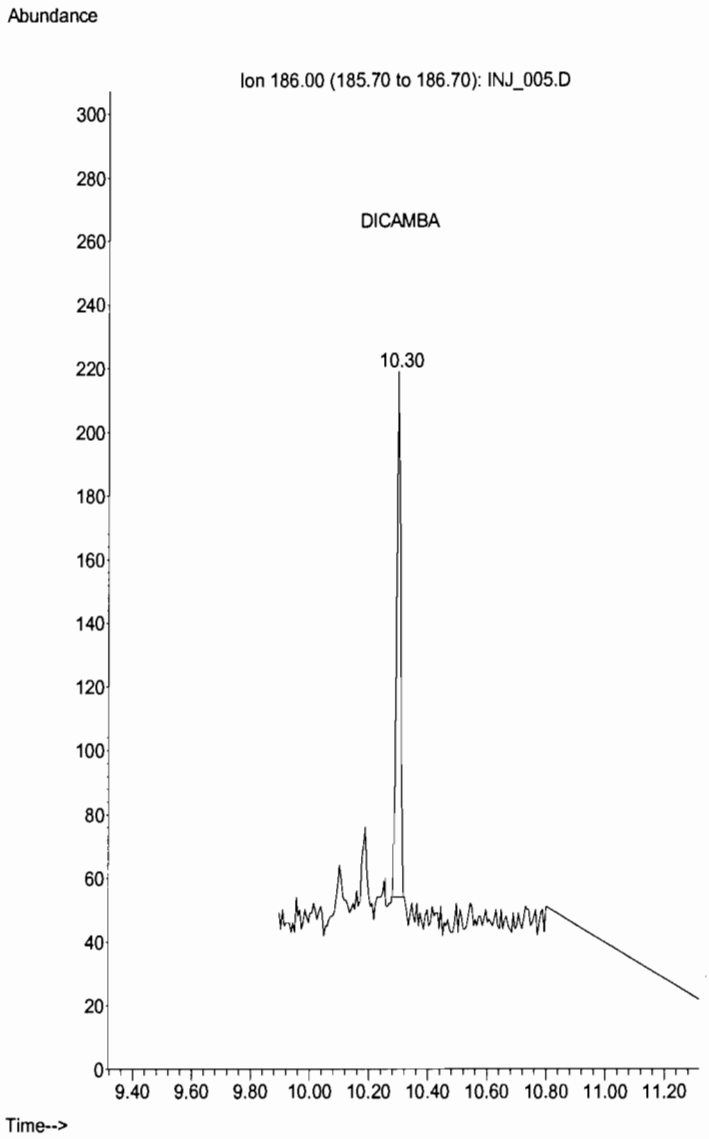
Figure 30 : Drinking water: Unfortified sample.
Sample concentration 25 mL mL^{-1}
Residue <LOQ Qualifier Ion *m/z* = 186



File					
Sample Name	06-1083/2			Type	Control
Field Name	dicamba-WATVAL-0003				
Study Number	T002102-06		Operator	Katherine White	
Sequence File	T1439.S		Method File	TNEGDIC_3.M	
			Vial	4	
Date Acquired	19 Oct 2006		19:45	Matrix Factor	1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
	Not Detected			

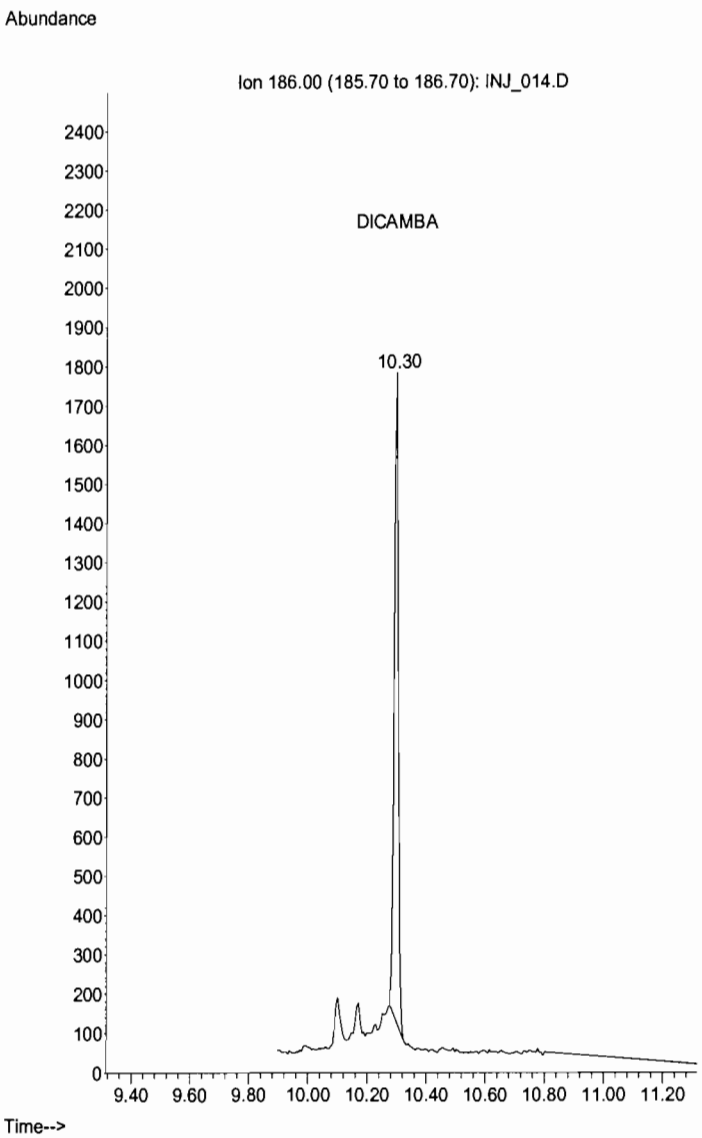
Figure 31 : Drinking water sample fortified with 0.05 µg L^{-1} dicamba. Sample concentration 25 mL mL^{-1}. Recovery = 86% Qualifier Ion *m/z* = 186



File					
Sample Name	06-1083/3			Type	Recovery
Field Name	dicamba-WATVAL-0003				
Study Number	T002102-06		Operator	Katherine White	
Sequence File	T1439.S		Method File	TNEGDIC_3.M	
			Vial	5	
Date Acquired	19 Oct 2006		20:08	Matrix Factor	1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	186	10.30	1608.5	100

Figure 32 : Drinking water sample fortified with 0.5 µg L^{-1} dicamba. Sample concentration 25 mL mL^{-1}. Recovery = 74% Qualifier Ion *m/z* = 186



File				
Sample Name	06-1083/8		Type	Recovery
Field Name	dicamba-WATVAL-0003			
Study Number	T002102-06	Operator	Katherine White	
Sequence File	T1439.S	Method File	TNEGDIC_3.M	
		Vial	10	
Date Acquired	19 Oct 2006	23:33	Matrix Factor	1.00000

Compound Name	Ion	RT (Mins)	Area	Ratio (%)
DICAMBA	186	10.30	16307.8	100

APPENDIX 5 DETECTOR LINEARITY GRAPHS

Figure 33: **GC-MSD Calibration Graph for dicamba (No Intercept Set). Target Ion *m/z* = 184**

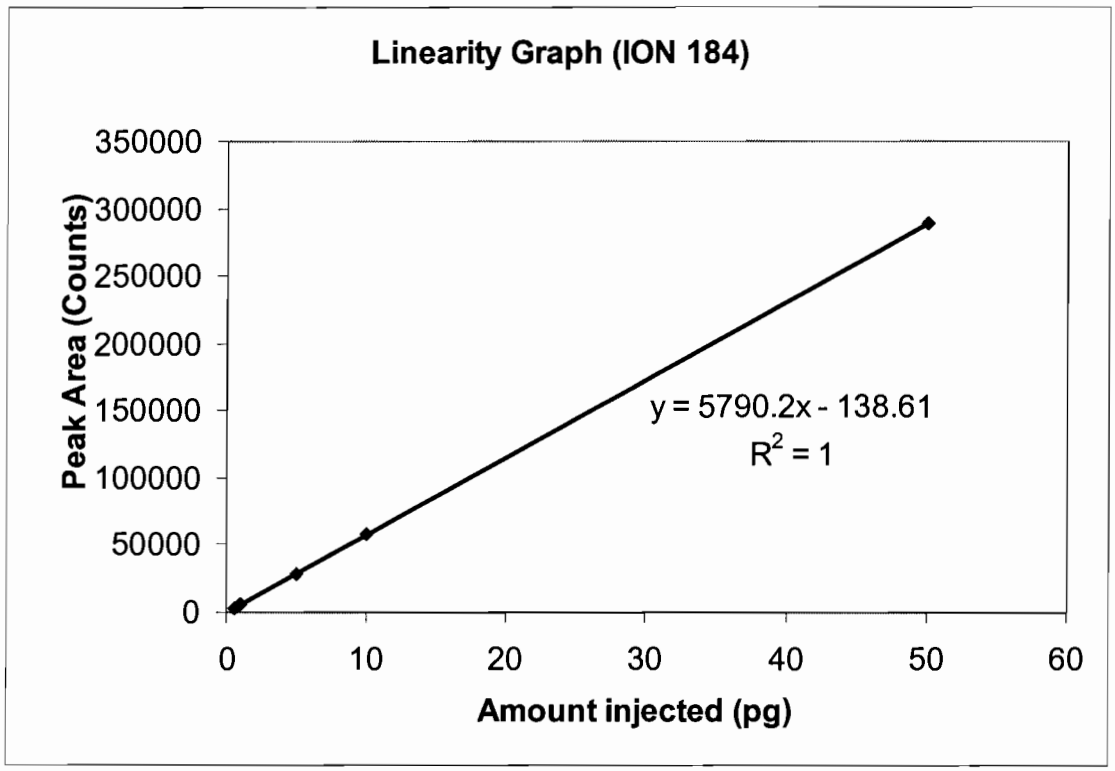


Figure 34: **GC-MSD Calibration Graph for dicamba (No Intercept Set) Qualifier Ion *m/z* = 185**

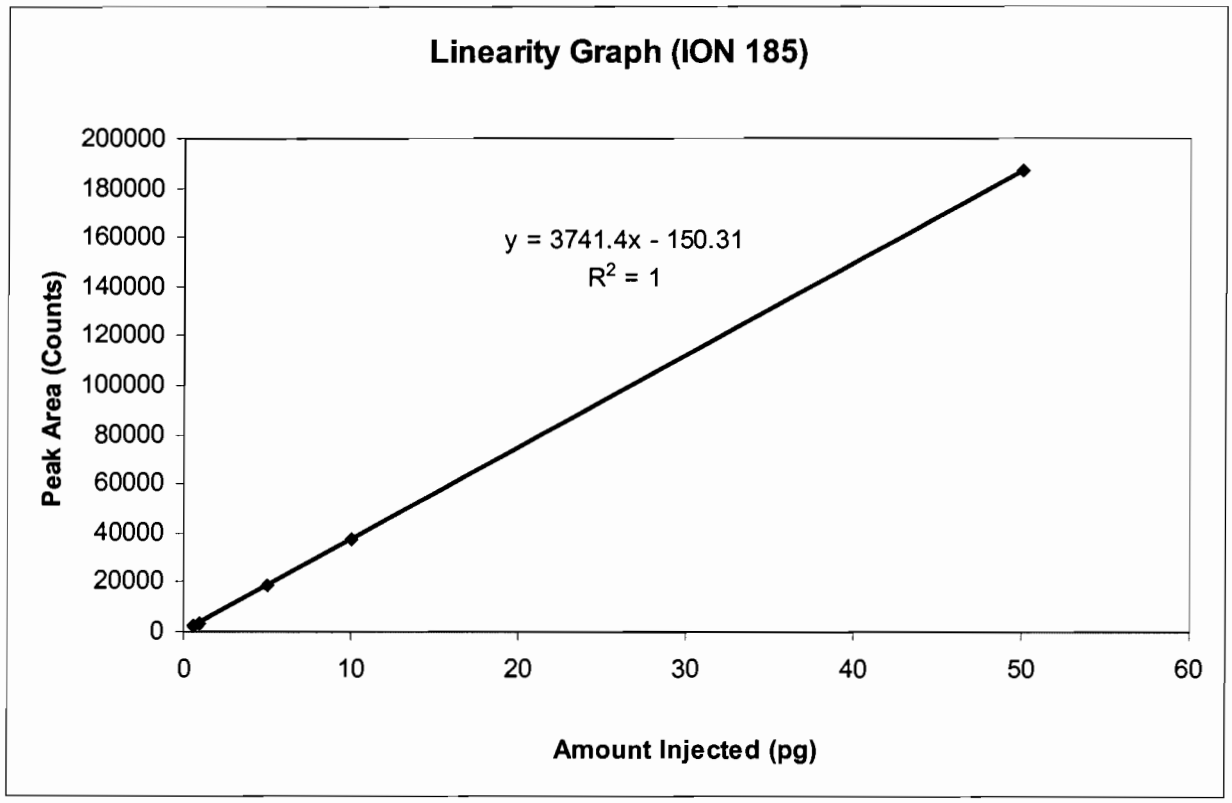
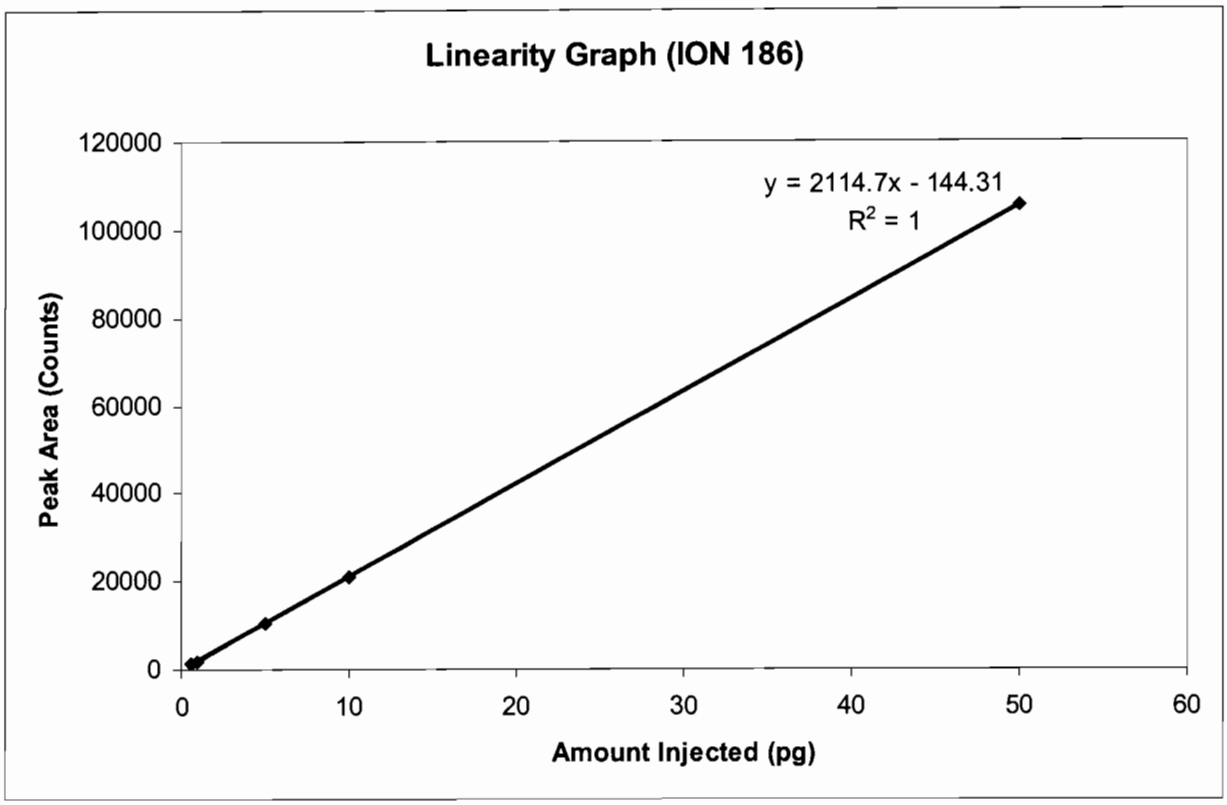


Figure 35: **GC-MSD Calibration Graph for dicamba (No Intercept Set) Qualifier Ion *m/z* = 186**

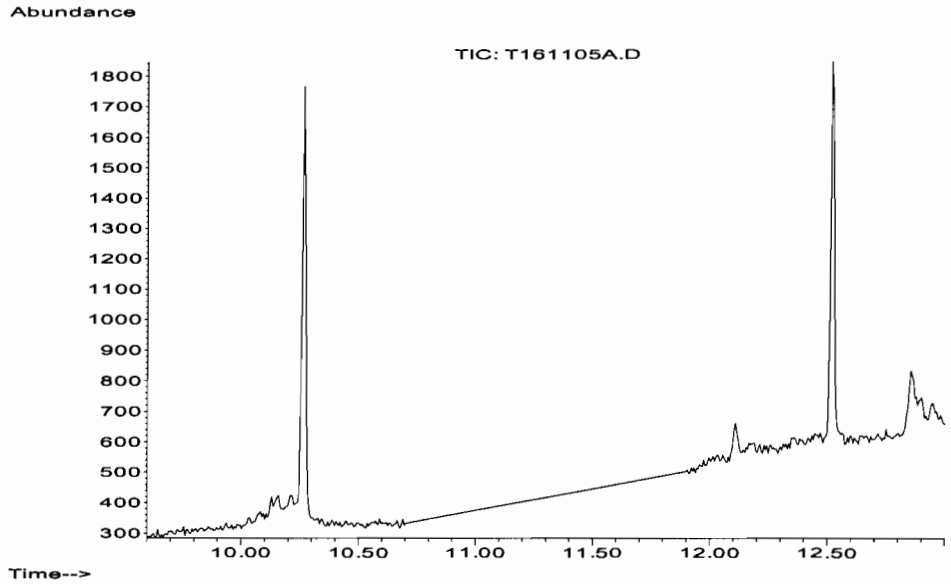


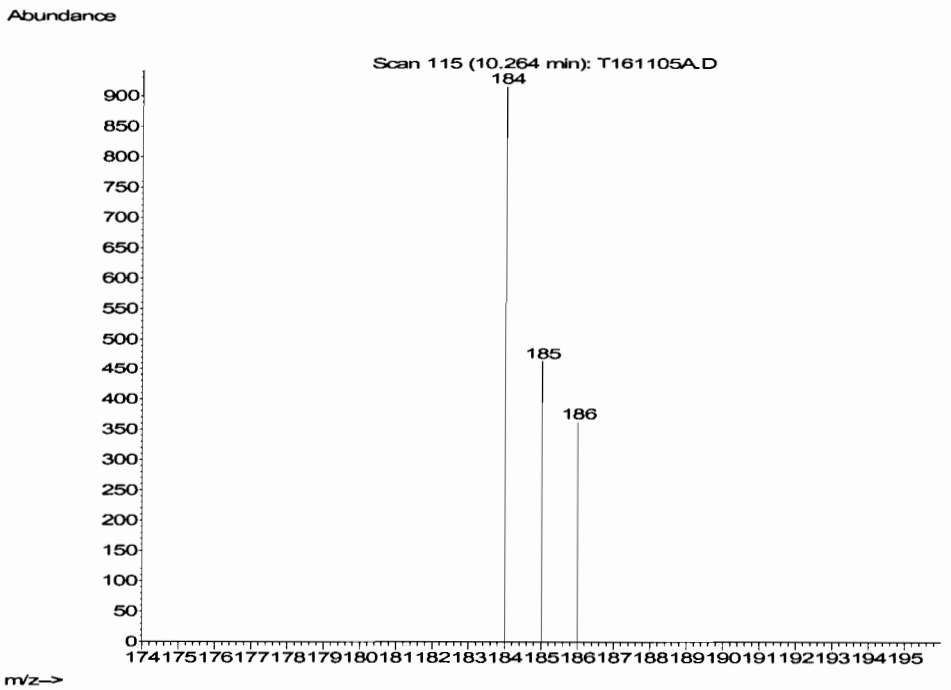
APPENDIX 6 GC-MSD FULL SCAN SPECTRA

Figure 36: Total Ion Chromatogram for Derivatised Dicamba In Negative Ion Chemical Ionisation Mode

The total ion chromatogram was not produced as part of the validation study.

GC-MSD: File no. T161105A. D





APPENDIX 7 METHOD FLOWCHART

Acidify water samples

↓

SPE concentration

↓

Derivatise with MTBSTFA

↓

Analysis by GC-MSD