Cover Sheet for

Environmental Chemistry Method

Pesticide Name: Linuron

MRID#: 470333-03

Matrix: Water

Analysis: LC/MS/MS

This method is provided to you by the Environmental Protection Agency=s (EPA) Environmental Chemistry Laboratory (ECL). This method *is not* an EPA method but one which was submitted to EPA by the pesticide manufacturer to support product registration. EPA recognizes that the methods may be of some utility to state, tribal, and local authorities, but makes no claim of validity by posting these methods. Although the Agency reviews *all* Environmental Chemistry Methods submitted in support of pesticide registration, the ECL evaluates only about 30% of the currently available methods in the laboratory. Most methods perform satisfactorily but some, particularly the older methods, have deficiencies. Moreover, the print quality of the methods varies considerably because the methods originate from different sources. Therefore, the methods offered represent the best available copies.

If you have difficulties in downloading the method, or further questions concerning the methods, you may contact Elizabeth Flynt at 228-688-2410 or via e-mail at flynt.elizabeth@epa.gov.

Study Title

ANALYTICAL METHOD FOR THE DETERMINATION OF DIURON, LINURON, AND METABOLITES IN WATER

Test Guidelines

European Commission, Directorate General Health and Consumer Protection. "Guidance Document on Residue Analytical Methods", SANCO/825/00 rev. 7, March 17, 2004

Author

Norbert Reichert

Date Study Completed

August 04, 2006

Performing Laboratory

SGS INSTITUT FRESENIUS GmbH
Im Maisel 14
D-65232 Taunusstein
Germany
Tel: 0049 6128 744 0

Project Identification Numbers

DuPont Study Number: DuPont-19220
SGS INSTITUT FRESENIUS Study Number: IF-06/00588606

STATEMENT OF NO DATA CONFIDENTIALITY CLAIMS

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA Section 10(d)(1)(A), (B), or (C).

Company: E. I. du Pont de Nemours and Company

Company Agent: Anna M. Stoops

U.S. Registration Coordinator
(Title)

Anna M Stoops
(Signature)

8-16-2006
(Date)

GOOD LABORATORY PRACTICE COMPLIANCE
STATEMENT OF COMPLIANCE

The study forming the subject of this report was performed under the supervision of the Study Director in accordance with the procedure described herein. The report provides an accurate record of the results obtained.

The study was conducted in compliance with the Principles of Good Laboratory Practices (GLP) as revised 1997 and set out in the OECD document OECD-DOC.ENV/MC/CHEM(98)17, Paris, 1998, with reference to the laws and regulations embodying these principles at the national level.

No circumstances were observed, which might have had an adverse influence on the integrity of the study.

Study Director

Dr. Norbert Reichert
SGS INSTITUT FRESENIUS GmbH

August 04, 2006
Date

Applicant/Sponsor

Anna M. Stoops Date: Aug 16, 2006
Authorized Agent of DuPont: Study Sponsor and Study Submitter

GLP CERTIFICATE OF SGS INSTITUT FRESENIUS

HESSISCHES MINISTERIUM
FÜR UMWELT, LÄNDLICHEN RAUM
UND VERBRAUCHERSCHUTZ

Gute Laborpraxis/Good Laboratory Practice

GLP-Bescheinigung/Statement of GLP Compliance
(gemäß/according to § 19b Abs. 1 Chemikaliengesetz)

Eine GLP-Inspektion zur Überwachung der Einhaltung der GLP-Grundsätze gemäß Chemikaliengesetz bzw. Richtlinie 88/320/EG wurde durchgeführt in

Assessment of conformity with GLP according to Chemikaliengesetz and Directive 88/320/EEC at:

☒ Prüfeinrichtung/Test facility ☐ Prüfstandort/Test site

Institut Fresenius Chemische und Biologische Laboratorien AG – GLP-Prüfeinrichtung
Im Maisel 14
65232 Taunusstein

(Unverwechselbare Bezeichnung und Adresse/Unequivocal name and adress)

Prüfungen nach Kategorien/Areas of Expertise
(gemäß/according chemVwV-GLP Nr. 5.3/OECD guidance)

1 Prüfungen zur Bestimmung der physikalisch-chemischen Eigenschaften und Gehaltsbestimmungen
4 Ökotoxikologische Prüfungen zur Bestimmung der Auswirkungen auf aquatische und terrestrische Organismen
5 Prüfungen zum Verhalten im Boden, im Wasser und in der Luft, Prüfungen zur Bioakkumulation und zur Metabolisierung
6 Prüfungen zur Bestimmung von Rückständen
9 Sonstige Prüfungen:
Analyse wertgebender Inhaltsstoffe (GVO)

1Physical and chemical properties and determination of content
4 Environmental toxicity studies on aquatic and terrestrial organisms
5 Behaviour in water soil and air, Bioaccumulation and metabolism
6 Residues
9 Other studies:
Nutritional Equivalence (GMO)

26.09.2002, 09. bis 11.12.2002, 19. und 24.02.2003
Datum der Inspektion/Date of Inspection
(Tag Monat Jahr/day month year)

Die genannte Prüfeinrichtung befindet sich im nationalen GLP-Überwachungsverfahren und wird regelmäßig auf Einhaltung der GLP-Grundsätze überwacht.

The above mentioned test facility is included in the national GLP Compliance Programme and is inspected on a regular basis.

Auf der Grundlage des Inspektionsberichtes wird hiermit bestätigt, dass in dieser Prüfeinrichtung die oben genannten Prüfungen unter Einhaltung der GLP- Grundsätze durchgeführt werden können.

Based on the inspection report it can be confirmed, that this test facility is able to conduct the aforementioned studies in compliance with the Principles of GLP.

Im Auftrag

Th. Zimmermann, Referent, Wiesbaden, den **08. Dezember 2003**
(Name und Funktion der verantwortlichen Person/
Name and function of responsible person)
Hess. Ministerium für Umwelt, ländlichen Raum und Verbraucherschutz, Mainzer Straße 80 D65189 Wiesbaden
(Name und Adresse der GLP-Überwachungsbehörde/Name and address of the GLP Monitoring Authority)

QUALITY ASSURANCE STATEMENT

Project Identification

SGS INSTITUT FRESENIUS Study Number: IF-06/00588606
DuPont Study Number: DuPont-19220

Study Title

Analytical Method for the Determination of Diuron, Linuron, and Metabolites in Water

Quality Assurance Statement

This final report was audited by the Quality Assurance Unit of SGS INSTITUT FRESENIUS in order to ensure the exact description of all methods, experiments, observations and results.

The study was inspected by the Quality Assurance Units of SGS INSTITUT FRESENIUS at the following dates:

Date of Inspection	*Date of the Inspection Report to the Study Director and the Head of the Test Facility*	*Object of the Inspection*
May 02, 2006	May 02, 2006	Study plan
May 03, 2006		Study plan - signature
June 26, 2006	June 26, 2006	Laboratory phase
July 05, 2006	July 05, 2006	Result tables
July 20, 2006	July 20, 2006	Draft report
August 03, 2006	August 03, 2006	Draft report
August 04, 2006		Final report

For the quality assurance unit.

Joerg Springer
SGS INSTITUT FRESENIUS GmbH
Quality Assurance Auditor

04 Aug. 2006
Date

CERTIFICATION
APPROVAL OF THE FINAL REPORT

ANALYTICAL METHOD FOR THE DETERMINATION OF DIURON, LINURON, AND METABOLITES IN WATER

We, the undersigned, declare that the work described in this report was performed under our supervision, and that this report provides an accurate record of the procedures and results.

Report by:

Dr. Norbert Reichert
Study Director

August 04, 2006
Date

Approved by:

Dr. A. Zumdick
Head of Test Facility

August 04, 2006
Date

BASIC STUDY INFORMATION

SGS INSTITUT FRESENIUS Study Number IF-06/00588606 entitled, "Analytical Method for the Determination of Diuron, Linuron, and Metabolites in Water"

TYPE OF STUDY:	Method Validation
SAMPLE MATRICES:	Drinking water (origin: ground water) and surface water
TEST ITEMS:	Diuron (DPX-14740), Linuron (DPX-Z0326), DCPMU (IN-15654), DCPU (IN-R0915), mCPDMU (IN-12894), desmethylated linuron (IN-Z0513)
SPONSOR:	E. I. du Pont de Nemours and Company Wilmington, Delaware 19898 U.S.A.
DUPONT STUDY MONITOR:	Frederick Q. Bramble, Jr. E. I. du Pont de Nemours and Company Wilmington, DE 19898
TEST FACILITY:	SGS INSTITUT FRESENIUS GmbH Im Maisel 14 D-65232 Taunusstein Germany Tel: 0049 6128 744 0
STUDY DIRECTOR AND CONTACT PERSON AT THE INDEPENDENT LABORATORY:	Dr. Norbert Reichert SGS INSTITUT FRESENIUS GmbH Address (see Test Facility) Tel: 0049 6128 744 801 FAX: 0049 6128 744 9204 e-mail: norbert.reichert@institut-fresenius.de

ANALYTICAL PHASE
TIMETABLE:

Study Initiation Date:	May 03, 2006
Experimental Start Date (validation):	June 06, 2006
Experimental Termination Date (validation):	June 26, 2006
Study Completion Date:	August 04, 2006

LIST OF ABBREVIATIONS AND SYMBOLS

%	percent
°C	degrees Centigrade
ESI	electrospray interface
HPLC	high-performance liquid chromatography
LC/MS	liquid chromatography/mass spectrometry
kg	kilogram
µg	microgram
min	minute
MS/MS	tandem mass spectrometry (2-stage mass analysis experiment)
m/z	mass/charge ratio
n	number
ng	nanogram
ppb	parts per billion
ppm	parts per million
rec	recovery
RF	Response Factor (analyte peak area / analyte concentration)
RSD	relative standard deviation (StDev / mean)
RSQ	r-squared; the square of the Pearson product moment correlation coefficient (determined using Excel® function RSQ)
sec	second
TIC	total ion chromatogram

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ANALYTICAL METHOD FOR THE DETERMINATION OF DIURON, LINURON, AND METABOLITES IN WATER

Norbert Reichert

1.0 ABSTRACT

An analytical method was developed for the determination of diuron, linuron, and metabolites DCPMU [3,4- N'-(3,4-dichlorophenyl)-N'-methylurea], DCPU [3,4-dichlorophenyl urea], mCPDMU [3-(3-chlorophenyl)-1,1-dimethylurea] and desmethylated linuron [N'-(3,4-dichlorophenyl)-N'-methoxyurea] in water. The target limit of quantitation (LOQ) for each analyte was 0.05 µg/L. The method was validated at 0.05 µg/L and 0.5 µg/L for all analytes. The extracts were analyzed using a LC/MS/MS system with an electrospray interface (ESI) operating in positive ion mode. The method was validated in two typical water sources (drinking equivalent to ground water and surface water).

Analytical Method

The water sample was filtered through paper and adjusted to 1% methanol . The sample was transferred onto a solid phase extraction cartridge (C18). The cartridge was rinsed with de-ionzed water. The analytes were eluted using methanol/de-ionized water (8+2, v+v). The eluate was concentrated by evaporation. The final extract was filtered prior to analysis by reverse phase HPLC online with ESI-LC/MS/MS for the determination of diuron, linuron, DCPMU, DCPU, mCPDMU, and desmethylated linuron.

The samples were extracted, cleaned-up using solid phase extraction, and typically analyzed overnight by LC/MS/MS. The time required for extraction, evaporation, and filtration of the final extracts prior to LC/MS/MS analysis was approximately 6 hours. A LC/MS/MS analytical run containing 7 standards and 13 samples took approximately 10 hours. The LC/MS/MS analysis was conducted unattended and could be run overnight.

Two specific MS/MS transitions of the molecular ion for each analyte were monitored. The total ion chromatogram (TIC) was used for quantitation and the relative responses of the two fragment ions for each analyte provided confirmatory analysis. Matrix interference was not observed in any of the water specimens examined.

The recoveries from water matrix samples fortified at 0.05 µg/L (LOQ) and 0.5 µg/L support the satisfactory performance of this method. The following tables summarize the average recovery results from the quantification MS/MS transition of samples fortified at two concentrations for drinking water and surface water, respectively.

VALIDATION DRINKING WATER - SUMMARY OF THE RESULTS

	QUANTIFICATION TRANSITION	NUMBER	LOQ 5	10-FOLD LOQ 5	OVERALL 10
DIURON	233 ≥ 72	Average (%)	100	100	100
		RSD (%)	7	7	6
LINURON	249 ≥ 160	Average (%)	88	95	91
		RSD (%)	4	5	6
DCPMU	219 ≥ 127	Average (%)	91	95	93
		RSD (%)	5	4	5
DCPU	205 ≥ 127	Average (%)	84	95	90
		RSD (%)	6	6	8
DESM. LINURON	235 ≥ 160	Average (%)	101	105	103
		RSD (%)	5	9	7
MCPDMU	199 ≥ 72	Average (%)	96	102	99
		RSD (%)	7	7	7

VALIDATION SURFACE WATER - SUMMARY OF THE RESULTS

	QUANTIFICATION TRANSITION	NUMBER	LOQ 5	10-FOLD LOQ 5	OVERALL 10
DIURON	233 ≥ 72	Average (%)	99	100	99
		RSD (%)	6	6	6
LINURON	249 ≥ 160	Average (%)	88	88	88
		RSD (%)	7	4	6
DCPMU	219 ≥ 127	Average (%)	91	93	92
		RSD (%)	7	3	5
DCPU	205 ≥ 127	Average (%)	97	95	96
		RSD (%)	7	7	7
DESM. LINURON	235 ≥ 160	Average (%)	95	89	92
		RSD (%)	8	2	7
MCPDMU	199 ≥ 72	Average (%)	89	84	86
		RSD (%)	5	3	5

2.0 INTRODUCTION

Diuron (DPX-14740) and linuron (DPX-Z0326) are active ingredients in phenylurea herbicides used to control broadleaf weeds and annual grasses in various field crops, fruit and nut crops, and noncrop areas. This method was developed to support the U.S. and EU re-registration and country specific registration effort for products containing linuron and diuron active ingredients. The method satisfies requirements in European Commission, Directorate General Health and Consumer Protection, "Guidance Document on Residue Analytical Methods", SANCO/825/00 rev. 7, March 17, 2004, and is intended as a regulatory method for the determination of residues in water matrices. DCPMU and DCPU are metabolites of linuron and diuron. The analyte mCPDMU is an anaerobic metabolite of diuron, and desmethylated linuron is a metabolite of linuron.

Water matrix subsamples are extracted using solid-phase extraction (SPE). The extract is concentrated by evaporation. The remaining extract is adjusted to final volume with methanol and filtered prior to the quantitative determination of linuron, diuron, DCPMU, DCPU, mCPDMU and desmethylated linuron by LC/MS/MS analysis. The analytical method was validated at the target method limit of quantitation (LOQ) of 0.05 µg/L and 0.5 µg/L (10×LOQ) for all analytes. The method limit of detection (LOD), based on the least responsive analyte, DCPU, was estimated to be 0.01 µg/L. Confirmatory analysis in this method is possible using relative ratio responses of two molecular ion fragments monitored for each of the analytes.

3.0 MATERIALS

Equivalent equipment and materials may be substituted unless otherwise specified; note any specifications in the following descriptions before making substitutions. Substitutions should only be made if equivalency/suitability has been verified with acceptable control and fortification recovery data.

3.1 Equipment

Analytical balance	Model BP 210 D, serial No 50707526 D95-09-011 – Sartorius
Water jet pump with Woulfe bottle	
Ultra pure water unit	Model Elix 3 UV and Milli-Q 185 Plus – Millipore
Vortex	Model Reax – Heidolph
Nitrogen evaporator	Model 112 and 111 – Organomation
Micro pipette	Model Microman, various sizes – Abimed Analysen-Technik
Centrifuge tube	Graduated glass tube with ground joint NS 14.5 , different sizes

Volumetric pipette	different sizes, quality "AS" or equivalent – Hirschmann or Brand
Pasteur pipette	different sizes
Volumetric flask	different sizes
Erlenmeyer flask	different sizes
Glass bottle	different sizes
Funnel	different sizes
Graduated cylinder	different sizes
Sample vial	1 mL with PTFE sealed crimp-on caps – CS-Chromatographie Service AG
Sample vial	40 mL
SPE manifold	Supelco
Reservoir	30 mL
Adapter	
Single use syringe	different sizes
Membrane filter	0.2 µm PTFE, Macherey-Nagel

HPLC

Unit	**Producer**	**Model**	**Serial No.**
Degasser	Agilent	G1322A	JP05033668
Pump	Agilent	G1311A	DE14918680
Injection system	CTC Analytics	HTS Pal	111374
Column oven with 6-portvalve	Agilent	G1316A	DE14927302
Control module	Agilent	G1323B	DE14903149

MS/MS

Unit	**Producer**	**Model**	**Serial No.**
LC-MS/MS	Applied Biosystems	API 3000	D10340204
Vacuum pump	Varian	DS602	205612
Data system	Applied Biosystems	Analyst, Version 1.4.1	

3.2 Reagents and Standards

3.2.1 Reagents

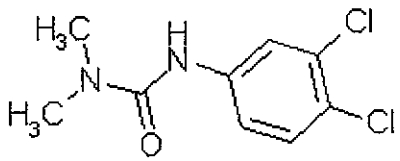
The equivalency/suitability of substituted reagents should be verified.

Methanol for HPLC	Part No. T169.1 – Roth
Deionized water	Produced by Elix 3UV/Milli-Q 185 Plus – Millipore
Formic acid	Part No. 1.00264 – Merck
Supelchem LC-18	0.5 g, 3 mL 57012 – Supelco
Folded filter paper, 185 mm diameter	Part No. 10311647 – Schleicher and Schuell

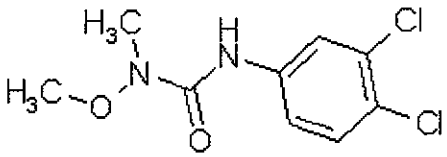
3.2.2 Reference Analytical Standards

The structures and specific information for diuron, linuron, DCPMU, DCPU, mCPDMU and desmethylated linuron are detailed below:

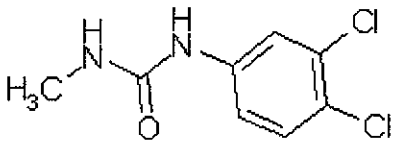
DPX-14740, Herbicide

Common Name	Diuron
C.A. Name:	N'-(3,4-dichlorophenyl)-N,N-dimethylurea
IUPAC Name:	3-(3,4-dichlorophenyl)-1,1-dimethylurea
CAS No.:	330-54-1
Structure:	
Lot (Dash):	235
DuPont Stock No.:	1002061
Appearance:	Solid powder
Date of Last Analysis:	23 April 2004
Purity:	98.7%
Storage Advice:	Room temperature at SGS INSTITUT FRESENIUS
Expiry Date:	23 April 2007

DPX-Z0326, Herbicide

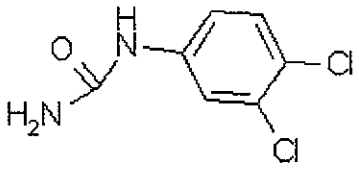
Common Name	Linuron
C.A. Name:	N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea
IUPAC Name:	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
CAS No.:	330-55-2
Structure:	
Lot:	236
DuPont Stock No.:	4004110
Appearance:	Solid
Date of Last Analysis:	18 Jan 2006
Purity:	99.9%
Storage Advice:	Room temperature at SGS INSTITUT FRESENIUS
Expiry Date:	18 Jan 2009

DCPMU (IN-15654)

Common Name	3,4-dichlorophenylmethylurea
C.A. Name:	N'-(3,4-dichlorophenyl)-N'-methylurea
IUPAC Name:	3-(3,4-dichlorophenyl)-1-methylurea
CAS No.:	3567-62-2
Structure:	
Lot:	012
DuPont Stock No.:	1000022
Appearance:	White powder
Date of Last Analysis:	25 July 2003
Purity:	99.9%
Storage Advice:	Room temperature at SGS INSTITUT FRESENIUS
Expiry Date:	24 July 2009

DCPU (IN-R0915)

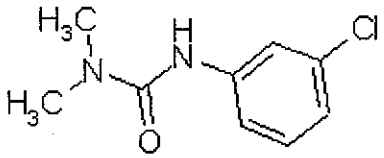
Common Name	3,4-dichlorophenylurea
C.A. Name:	3,4-dichlorophenyl urea
IUPAC Name:	N-(3,4-dichlorophenyl)urea
CAS No.:	2327-02-8
Structure:	



Lot (Dash):	008
DuPont Stock No.:	1001368
Appearance:	Solid powder
Date of Last Analysis:	22 October 2004
Purity:	99.9%
Storage Advice:	Room temperature at SGS INSTITUT FRESENIUS
Expiry Date:	22 October 2010

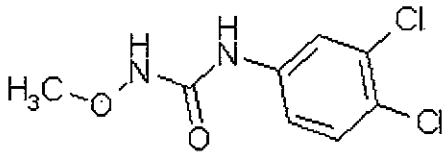
mCPDMU (IN-12894)

Common Name	chlorophenyldimethylurea
C.A. Name:	N'-(3-chlorophenyl)-N,N-dimethyl urea
IUPAC Name:	3-(3-chlorophenyl)-1,1-dimethylurea
CAS No.:	587-34-8
Structure:	



Lot (Dash):	004
Stock No.:	1001187
Appearance:	Solid powder
Date of Last Analysis:	24 February 2004
Purity:	99.1%
Storage Advice:	Room temperature at SGS INSTITUT FRESENIUS
Expiry Date:	24 February 2007

desmethylated-linuron (IN-Z0513)

Common Name	3,4-dichlorophenylmethoxyurea
C.A. Name:	N'-(3,4-dichlorophenyl)-N'-methoxyurea
IUPAC Name:	1-(3,4-dichlorophenyl)-3-methoxyurea
CAS No.:	17356-61-5
Structure:	
Lot (Dash):	001
DuPont Stock No.:	1000759
Appearance:	Solid
Date of Last Analysis:	08 September 2004
Purity:	99.8%
Storage Advice:	Room temperature at SGS INSTITUT FRESENIUS
Expiry Date:	08 September 2010

3.3 Safety and Health

Each analyst must be acquainted with the potential hazards of the reagents, products, and solvents used in this method before commencing laboratory work. All appropriate material safety data sheets should be read and followed, and proper personal protective equipment should be used.

4.0 METHODS

4.1 Principle of the Analytical Method

This method was developed for the determination of diuron, linuron, DCPMU, DCPU, mCPDMU and desmethylated linuron in water matrices to support regulatory studies. The method was validated in drinking and surface water for all analytes at a target LOQ of 0.05 µg/L and 0.5 µg/L (10×LOQ).

A 0.2 mL aliquot of methanol was added to 20 mL of paper filtered water sample. A solid phase extraction cartridge (reversed phase, C-18) was conditioned with 5 mL of methanol and 2×5 mL of de-ionized water (the cartridge was not allowed to go to dryness). The sample was eluted through the cartridge. The cartridge was rinsed twice with de-ionzed water (2 mL each) and dried using vacuum. A 0.5 mL aliquot of methanol/de-ionized water (8+2, v+v) was added to the cartridge and incubated on column for 2 minutes without applied vacuum. The analytes were eluted using 2 mL of methanol/de-ionized water (8+2, v+v) into a graduated centrifuge tube. The eluate was concentrated by evaporation using a gentle stream of nitrogen (water bath temperature 40°C) to a volume below 1 mL. The extract was diluted with methanol to a final volume of 1 mL and subsequently filtered (0.2 µm) prior to analysis by

reverse phase HPLC online with ESI-LC/MS/MS for the determination of linuron, diuron, DCPMU, DCPU, mCPDMU, and desmethylated linuron. Quantitative analysis is accomplished using the total ion chromatogram (TIC) from two molecular ion transitions for each analyte. The relative abundance of the MS/MS fragment ions provides confirmatory evidence for each analyte.

4.2 Analytical Procedure

4.2.1 Glassware & Equipment Cleaning Procedures

The effectiveness of any cleaning procedure used should be demonstrated by preparation and analysis of reagent blanks. In general, all reusable glassware and plasticware should be washed in hot tap water with laboratory grade detergent, rinsed several times with tap water, rinsed several times with deionized water, rinsed once with acetone, and allowed to fully dry before use. Care should be taken to avoid working with high levels of the analyte in the same laboratory where samples are being extracted and analyzed.

4.2.2 Preparation & Stability of Reagent Solutions

Aqueous 0.2% formic acid solution
Add 2 mL of formic acid to 998 mL of de-ionized water and mix.

Solution for SPE elution (methanol/de-ionized water)
Add 80 mL of methanol to 20 mL of de-ionized water and mix.

4.2.3 Stock Standard Preparation and Stability

If possible, use standards with purity greater than 95%. A minimum of approximately 10 mg of standard should be weighed on an analytical balance that provides a weight precision to three significant figures, or the amount of standard should be increased to satisfy this condition.

Individual stock solutions for diuron, linuron, DCPMU, DCPU, mCPDMU, and desmethylated linuron are prepared at a target concentration of 1 mg/mL in methanol. For example, 1 mg/mL stock standards can be prepared by weighing approximately 10 mg (adjusted for purity) of analyte in a tared 10-mL volumetric flask. The volumetric flasks are diluted to volume in methanol, capped, and well-shaken to prepare stock solutions. These solutions are stored at or below 4°C and are stable for at least six months. Stock standards use may be extended if supported by stability test data.

A 1 mL aliquot of each stock solution was transferred into a 10 mL volumetric flask. The flask was diluted to 10 mL with methanol. The concentration for each analyte was approximately 100 µg/mL in the standard mixture solution (SM).

4.2.4 *Fortification Standard Preparation and Stability*

Fortification solutions are prepared from dilutions of the 100 µg/mL standard mixture solution (SM).

0.1 µg/mL Fortification Solution
Dilute the 100 µg/mL SM with methanol/de-ionized water/0.2% formic acid (30+70+0.2, v+v+v) to a concentration of approximately 0.1 µg/mL for each analyte.

0.02 µg/mL Fortification Solution
Dilute the 100 µg/mL SM with methanol/de-ionized water/0.2% formic acid (30+70+0.2, v+v+v) to a concentration of approximately 0.02 µg/mL for each analyte.

Fortification Standards use may be extended if supported by stability test data.

4.2.5 *Calibration Standard Preparation and Stability*

Calibration standards are prepared from dilutions of 100 µg/mL standard mixture solution (SM). A minimum of five calibration standards over a range from ≤30% of LOQ equivalent final concentration to ≥120% of the highest expected final sample concentration analyzed are required for quantification. Seven or more calibration standards are recommended.

For example, calibration standard of 15 ng/mL can be prepared from the 0.1 µg/mL (100 ng/mL) fortification solutions, by diluting a 3 mL aliquot to final volume of 20.0 mL in methanol/de-ionized water/0.2% formic acid (30+70+0.2, v+v+v). This standard is further diluted in methanol/de-ionized water/0.2% formic acid (30+70+0.2, v+v+v) using pipettes according to the following table to prepare 0.3, 0.5, 1.0, 2.5, 5.0 and 10.0 ng/mL calibration solutions.

Code of standard	Aliquot (mL)	Dilute from	Final volume (mL)	Analyte (ng/mL)
Mix E	-	-	-	100
Mix F	3	Mix E	20	15
Mix G	2.5	Mix E	25	10
Mix H	1	Mix E	20	5
Mix K	5	Mix G	20	2.5
Mix L	2	Mix G	20	1
Mix M	1	Mix G	20	0.5
Mix N	3	Mix L	10	0.3

Calibration standards can be prepared concurrently with sample fortifications using this procedure.

4.2.6 *Source (& Characterization) of Samples*

The drinking water sample (tap water generated from ground water) was taken at SGS INSITUT FRESENIUS in D-65232 Taunusstein.

The surface water sample was taken from a ditch in D-65549 Limburg.

The samples were natural water specimens (drinking and surface water). The surface water specimen was transported in polyethylene bottles. During sampling the air temperature was about 20°C. The specimen arrived in good condition on June 07, 2006 and were stored until analysis at -18°C. The drinking and surface samples were given individual internal specimen identification. The surface water specimens were characterised by pH-value, conductivity, total organic carbon. The measurement of the conductivity is based on the DIN EN 27888*. The determination of the TOC is based on the DIN EN 1484†. The chemicals and the equipment used for the characterisation are specified in the raw data of the study.

Surface water

Specimen code:	010/6202452
Name of the river:	Großbach
Location:	D-65549 Limburg (Hesse)
pH-value:	8.03
Conductivity:	759 µs/cm
Total organic carbon:	5.4 mg/L

Drinking water

Specimen code:	010/6202451
Location:	D-65232 Taunusstein. (Hesse)
pH-value:	7.75
Conductivity:	503 µs/cm
Total organic carbon:	2.3 mg/L

4.2.7 *Sample Fortification Procedure*

Fortify aliquots (20 mL) of the water samples as required. The following table is provided as an example for fortification levels used in this study.

FORTIFICATION LEVEL (µG/L)	CONCENTRATION OF FORTIFICATION SOLUTIONS (µG/ML)	FORTIFICATION SOLUTION ALIQUOT (ML)
0.05	0.02	0.05
0.50	0.10	0.10

Shake the samples after fortification.

* Determination of the electrical conductivity (ISO 7888:1985) DIN EN 27888:1993

† Determination of total organic carbon (TOC) and the dissolved organic carbon (DOC) DIN EN 1484: 1997

4.2.8 *Analyte Extraction Procedure*

1. Filter the water sample through a folded filter paper, if necessary.
2. Connect solid-phase cartridge (SPE) to vacuum manifold (water jet pump with Woulfe bottle). Rinse the cartridge subsequently with 5 mL of methanol and twice with 5 mL of de-ionized water, each. Do not allow cartridge to go to dryness. Mount a reservoir on top of the SPE cartridge.
3. Fortify aliquots (20 mL) of the control samples as required. Add 0.2 mL of methanol to the sample and mix.
4. Transfer the sample onto the SPE cartridge and elute the sample through the cartridge using vacuum. Rinse the cartridge using 2x2 mL of de-ionized water. Continue vacuum until cartridge is completely dry (approximately 10 minutes).
5. Break vacuum and transfer 0.5 mL of methanol/de-ionized water (80+20, v+v) onto the cartridge and incubate for 2 minutes with only gravity elution. Elute the analytes with 2 mL of methanol/de-ionized water (80+20, v+v).
6. Evaporate the eluate to less than 1 mL by means of a gentle stream of nitrogen. Dilute the extract with methanol to a final volume of 1 mL. Dilute the extracts of the 10-fold LOQ fortification to a calculated final volume of 10 mL. Filter (0.2 µm PTFE) an aliquot for LC/MS/MS analysis.

4.3 ***Instrumentation***

The following analytical conditions were used.

HPLC-Conditions

Unit	**Producer**	**Model**	**Serial No.**
Degasser	Agilent	G1322A	JP05033668
Pump	Agilent	G1311A	DE14918680
Injection system	CTC Analytics	HTS Pal	111374
Column oven with 6-portvalve	Agilent	G1316A	DE14927302
Control module	Agilent	G1323B	DE14903149

Column	**Analytical Column**
Length×ID [mm×mm]	150×3.0
Sorbent	HYPURITY C8
Particle size [µm]	5.0
Producer/supplier	Thermo
internal IF-no.	225

Eluent (channel) A	-
Eluent (channel) B	-
Eluent (channel) C	Methanol
Eluent (channel) D	0.2% formic acid

Gradient Program

Time [min]	Flow [mL/min]	Eluent C [%]	Eluent D [%]
0.00	0.5	30	70
10.00	0.5	90	10
15.00	0.5	99	1
15.10	0.5	99	1
17.10	0.5	30	70
23.00	0.5	30	70

Oven temperature [°C]	40	Switching intervals	
Injection volume [µL]	20	to waste [min]	from 0 to 5
Temperature of sample thermostat [°C]	10	to LC-MS/MS [min]	from 5 to 11
Post-column Split (detector/waste)	1:1	to waste [min]	from 11 to 23

MS/MS-Conditions

Unit	Producer	Model	Serial No.
LC-MS/MS	Applied Biosystems	API 3000	D10340204
Vacuum pump	Varian	DS602	205612
Data system	Applied Biosystems	Analyst, Version 1.4.1	

Turbo Ion Spray	Position	Resolution
X-axis	5	Q1
Y-axiy	-1	Q3
Nebulizer (gas)	10	
Curtain gas, nitrogen	9	
Collision gas, nitrogen	7	
Auxiliary (gas 2),	5500	

Scanning Method

Period	1	1	1	1
Experiment	1	1	1	1
Retention window [min]	0-23	0-23	0-23	0-23
Ion spray voltage [V]	5500	5500	5500	5500
Temperature [°C]	350	350	350	350
Analyte	Diuron	Diuron	Linuron	Linuron
Ionisation mode	ES+	ES+	ES+	ES+
Scan type	MRM	MRM	MRM	MRM
Q1 Mass [amu]	233	233	249	249
Q3 Mass [amu]	72	46	160	182
Declustering potential [V]	35	35	30	30
Focusing potential [V]	140	140	110	110
Collision energy [V]	37	33	33	19
Collision cell exit pot [V]	2	10	10	12
Entrance potential [V]	10	10	10	10
Ion energy 1 [V]	1.000	1.000	1.000	1.000
Ion energy 3 [V]	0.400	0.400	0.400	0.400
Dwell [msec]	100	100	100	100
Deflector [V]	-220	-220	-220	-220
Channel electron multiplier [V]	2300	2300	2300	2300

Scanning Method

Period	1	1	1	1
Experiment	1	1	1	1
Retention Window [min]	0-23	0-23	0-23	0-23
Ion spray voltage [V]	5500	5500	5500	5500
Temperature [°C]	350	350	350	350
Analyte	DCPMU	DCPMU	DCPU	DCPU
Ionisation mode	ES+	ES+	ES+	ES+
Scan type	MRM	MRM	MRM	MRM
Q1 Mass [amu]	219	219	205	205
Q3 Mass [amu]	127	162	127	162
Declustering potential [V]	30	30	30	30
Focusing potential [V]	140	140	120	120
Collision energy [V]	37	23	35	21
Collision cell exit pot [V]	8	10	10	10
Entrance potential [V]	10	10	10	10
Ion energy 1 [V]	1.000	1.000	1.000	1.000
Ion energy 3 [V]	0.400	0.400	0.400	0.400
Dwell [msec]	100	100	100	100
Deflector [V]	-220	-220	-220	-220
Channel electron multiplier [V]	2300	2300	2300	2300

Period	1	1	1	1
Experiment	1	1	1	1
Retention window [min]	0-23	0-23	0-23	0-23
Ion spray voltage [V]	5500	5500	5500	5500
Temperature [°C]	350	350	350	350
Analyte	Des.-linuron	Des.-linuron	mCPDMU	mCPDMU
Ionisation mode	ES+	ES+	ES+	ES+
Scan type	MRM	MRM	MRM	MRM
Q1 Mass [amu]	235	235	199	199
Q3 Mass [amu]	160	161	72	46
Declustering potential [V]	30	30	35	35
Focusing potential [V]	120	120	130	130
Collision energy [V]	25	27	35	29
Collision cell exit pot [V]	10	8	2	6
Entrance potential [V]	10	10	10	10
Ion energy 1 [V]	1.000	1.000	1.000	1.000
Ion energy 3 [V]	0.400	0.400	0.400	0.400
Dwell [msec]	100	100	100	100
Deflector [V]	-220	-220	-220	-220
Channel electron multiplier [V]	2300	2300	2300	2300

Approximate Analyte Retention Times:

diuron =	8.7 min
linuron =	9.4 min
DCPMU =	8.6 min
DCPU =	8.2 min
mCPDMU =	6.9 min
Desm. linuron =	8.7 min

4.3.1 *Calibration Procedures*

Use standard mass spectrometer tuning and calibration techniques. If confidence in the mass calibration needs to be established (modern mass spectrometers under digital control generally do not need frequent mass calibration, especially for quantitative modes), use vendor recommended calibrating solution. Optimization tuning of MS system may be accomplished by infusion of one or more of the test analytes. This method uses external standards, prepared as described in Section *4.2.5*.

Linear regression without weighting was used. The linear regression response of external calibration standards using Excel® functions SLOPE, INTERCEPT, and RSQ were monitored to establish calibration curve linearity. Acceptance criteria for valid quantitation was: R value (correlation coefficient) >0.99.

The instrument calibrated range was 0.3 ng/mL (0.3 × LOQ of 0.010 µg/L equivalent final concentration) to 15.0 ng/mL with 20 µL injection volume. Generally, seven calibration solutions were analyzed for quantitative LC/MS/MS analysis (a minimum of five calibration solutions are required).

Net recoveries may be calculated for fortified samples only (not acceptable for field samples). Net recoveries may be calculated and reported only when residues in the control sample are integrable and <30% of the LOQ. When the control residues are >30% of the LOQ, the recovery samples prepared at the LOQ using that control are invalidated. When the control residues are <30% of the LOQ, corrected µg/L found in fortified samples are calculated by subtracting area counts found in the control from area counts found in fortified samples. If net recoveries are calculated, those results must be uniquely identified or presented in a separate spreadsheet column heading for corrected µg/L.

4.3.2 *Sample Analysis*

Preliminary runs of at least two calibration standards or control sample extracts are routinely made to insure the LC/MS/MS system is equilibrated. If multiple sets are analyzed, a solvent blank injection should be made between the last and first injections of the sets to minimize risk of carryover between sets. Calibration standard analyses should precede the first sample analysis and follow the last sample analysis so sample analyses are contained within the external standard calibration. Generally, the injection sequence was organized from lowest to highest expected analyte concentrations. Calibration standard runs were intermixed with the test samples and

should be analyzed before and after every 3–4 samples in each analytical set. Extracts and calibration standards should be refrigerated if stored. Generally, fortification sample recoveries (70-110%) are required for acceptable quantitation results in a analysis set.

4.4 Calculations

4.4.1 Methods

Diuron, linuron, DCPMU, DCPU, mCPDMU and desmethylated linuron residues were measured as µg/L in water.

The detector signals were registered and integrated using the data systems outlined in section MS/MS conditions. The peak area was taken into account to determine the analyte amounts in the specimens. The calibration curves were calculated from the peak area of the calibration solutions and the corresponding amount of the analyte injected using equation (1).

(1) $y = a + bx$

where:

- y: peak area [integration units iu/sec]
- x: amount of the analyte injected [ng]
- a: ordinate intercept [iu]
- b: slope [iu/ng]

The amount injected (ng) of the analyte in the specimen was calculated using the transformed equation (1):

(2) $x = \frac{y - a}{b}$

The concentration C of the analyte in the specimen was calculated from x using equation (3):

(3) $C = \frac{x \cdot V_E \cdot}{V_i \cdot W} \times \frac{1\mu g}{1000 ng} \times \frac{10^6 \mu L}{L}$

where:

- x: amount of the analyte injected (ng)
- C: analysed concentration of the analyte in the specimen (µg/L)
- V_E: final volume (1 or 10 mL)
- V_i: injection volume (20 µL)
- W: specimen volume (20 mL)

The recovery data was calculated according to equation (4):

$$(4)\ R = \frac{C \cdot 100}{C_{for}}$$

where:

R: recovery [%]

C: analysed concentration of the analyte in the fortified specimen (µg/L)

C_{for}: nominal concentration of the analyte in the fortified specimen (µg/L)

An example calculation is shown below for diuron using water sample 010/6202451-A extracted and analyzed on June 23, 2006. This sample was fortified with 0.050 µg/L of diuron. The peak area of the diuron peak was 24087 integration units iu/sec.

Calibration:

(1) $y = 1100 + 1188649.98x$

The amount of the analyte in the specimen injected was calculated using the transformed equation (1):

$$(2)\ \frac{24087 - 1110}{1188649.98} = 0.0193\,\text{ng}$$

The concentration C of the analyte in the specimen was calculated from x using equation (3):

$$(3)\ C = \frac{0.0193 \cdot 1}{20 \cdot 20} \times 1000 = 0.048 \mu g / L$$

where:

x: amount of the analyte injected (0.0193 ng)

C: analysed concentration of the analyte in the specimen (0.048 µg/L)

V_E: final volume (1 mL)

V_i: injection volume (20 µL)

W: specimen volume (20.03 mL)

The recovery data was calculated according to equation (4):

(4) $$R = \frac{0.048 \cdot 100}{0.05017} = 96\ \%$$

where:

R: recovery [%]

C: analysed concentration of the analyte in the fortified specimen (0.048 µg/L)

C_{for}: nominal concentration of the analyte in the fortified specimen (0.05017 µg/L)

The recovery values reported represent rounded results which were obtained from calculations based on the exact raw data. The detector signals of the control specimens (if any) were subtracted from the fortified specimens.

5.0 RESULTS AND DISCUSSION

5.1 Method Validation Results

5.1.1 Detector Response

A triple quadrupole mass spectrometer using an ESI in positive ion mode and tandem mass spectrometry detection was used for instrumental analysis. Full-scan mass spectra acquired by LC/MS/MS from individual analyte on-column analysis for diuron, linuron, DCPMU, DCPU, mCPDMU and desmethylated linuron are provided in Figure 1 through Figure 6, respectively.

For each analyte, calibration standards typically yielded a linear response (r^2>0.99) over the range of 0.3 to 15 ng/mL (0.006 to 0.3 ng injected). Representative calibration curves for each analyte were constructed using calibration standards from a validation set and are presented in Figure 7 to Figure 12. Representative chromatograms of calibration standards are provided for diuron, linuron, DCPMU, DCPU, mCPDMU and desmethylated linuron in Figure 13 to Figure 18 and Figure 43 to Figure 48. Representative chromatograms from a reagent blank are provided for each analyte in Figure 19 to Figure 24.

Representative chromatograms of extracts from a control sample, a 0.05 µg/L (LOQ) fortification sample and a 0.5 µg/L fortification sample for each water matrix are provided in Figure 25 to Figure 42 (drinking water) and Figure 55 to Figure 72 (surface water).

5.1.2 Controls

No significant matrix interference was observed in the regions of diuron, linuron, DCPMU, DCPU, mCPDMU and desmethylated linuron elution in chromatograms of the extracts of control water samples.

5.1.3 Recoveries (Accuracy & Precision)

Representative recovery results are provided in Tables 1 to 6 for drinking water and Tables 7 to 12 for surface water. Summaries of average results for quantitation and confirmation MS/MS transitions of each analyte at the 0.05 µg/L (LOQ) and 0.5 µg/L (10×LOQ) fortification levels with overall results in each matrix are provided in the following tables.

VALIDATION DRINKING WATER – SUMMARY OF THE RESULTS

	QUANTIFICATION TRANSITION	NUMBER	LOQ 5	10-FOLD LOQ 5	OVERALL 10
DIURON	233 ≥ 72	Average (%)	100	100	100
		RSD (%)	7	7	6
LINURON	249 ≥ 160	Average (%)	88	95	91
		RSD (%)	4	5	6
DCPMU	219 ≥ 127	Average (%)	91	95	93
		RSD (%)	5	4	5
DCPU	205 ≥ 127	Average (%)	84	95	90
		RSD (%)	6	6	8
DESM. LINURON	235 ≥ 160	Average (%)	101	105	103
		RSD (%)	5	9	7
MCPDMU	199 ≥ 72	Average (%)	96	102	99
		RSD (%)	7	7	7

	CONFIRMATION TRANSITION	NUMBER	LOQ 5	10-FOLD LOQ 5	OVERALL 10
DIURON	233 ≥ 46	Average (%)	92	92	92
		RSD (%)	5	6	5
LINURON	249 ≥ 182	Average (%)	99	105	102
		RSD (%)	6	6	6
DCPMU	219 ≥ 162	Average (%)	94	104	99
		RSD (%)	7	7	8
DCPU	205 ≥ 162	Average (%)	81	93	87
		RSD (%)	2	9	9
DESM. LINURON	235 ≥ 161	Average (%)	104	105	104
		RSD (%)	4	3	4
MCPDMU	199 ≥ 46	Average (%)	85	98	92
		RSD (%)	5	9	10

VALIDATION SURFACE WATER - SUMMARY OF THE RESULTS

	QUANTIFICATION TRANSITION	NUMBER	LOQ 5	10-FOLD LOQ 5	OVERALL 10
DIURON	233 ≥ 72	Average (%)	99	100	99
		RSD (%)	6	6	6
LINURON	249 ≥ 160	Average (%)	88	88	88
		RSD (%)	7	4	6
DCPMU	219 ≥ 127	Average (%)	91	93	92
		RSD (%)	7	3	5
DCPU	205 ≥ 127	Average (%)	97	95	96
		RSD (%)	7	7	7
DESM. LINURON	235 ≥ 160	Average (%)	95	89	92
		RSD (%)	8	2	7
MCPDMU	199 ≥ 72	Average (%)	89	84	86
		RSD (%)	5	3	5

	CONFIRMATION TRANSITION	NUMBER	LOQ 5	10-FOLD LOQ 5	OVERALL 10
DIURON	233 ≥ 46	Average (%)	101	99	100
		RSD (%)	4	4	4
LINURON	249 ≥ 161	Average (%)	94	85	89
		RSD (%)	7	3	8
DCPMU	219 ≥ 162	Average (%)	99	99	99
		RSD (%)	5	7	5
DCPU	205 ≥ 162	Average (%)	101	99	100
		RSD (%)	6	9	8
DESM. LINURON	235 ≥ 161	Average (%)	101	87	94
		RSD (%)	6	10	11
MCPDMU	199 ≥ 46	Average (%)	92	86	89
		RSD (%)	8	4	7

Representative results from individual sample set analyses for each commodity are provided in Figure 31 to Figure 42 (drinking water) and Figure 61 to Figure 72 (surface water).

5.1.4 *Limit of Quantitation (LOQ)*

The LOQ determined in this method was 0.05 µg/L in water matrix. The LOQ is defined as the lowest fortification level at which average recoveries of 70-110% and a RSD <20% are achieved. In addition at this fortification level, the analyte peak consistently represents a signal-to-noise ratio of approximately 11–32 to 1 for all analytes. For the standard solution 0.5 ng/mL (50% of LOQ) the signal-to-noise ratio is in the range of 5–20 to 1.

5.1.4.a *Background Evaluation*

Background levels experienced in tandem mass spectrometry analyses are minimal. Generally, the chromatographic profiles of a sample extract solution and a calibration standard solution appear the same. The control sample chromatograms for the water samples tested are provided in Figure 25 to Figure 30 (drinking water) and Figure 55 to Figure 60 (surface water).

5.1.5.4 *Limit of Detection (LOD)*

A method limit of detection (LOD) was estimated to be 0.01 µg/L based on the limiting response analyte, DCPU. The LOD is defined as the analyte concentration in matrix with a response equivalent to a signal-to-noise ratio of approximately 3 to 1. The LOD was estimated from the signal to noise response of each analyte in matrix at LOQ level using the following equation.

$$\frac{LOD\ signal\ to\ noise\ response\ (3/1)}{Observed\ LOQ\ signal\ to\ noise\ reponse}\ x\ LOQ = \frac{3/1}{11/1}\ x\ 0.05\ \mu g/L = 0.01\ \mu g/L$$

Variation in the LOD was observed and each lab using this method should estimate an LOD value.

5.2 ***Timing***

Generally, samples were extracted using SPE and subsequently analyzed by LC/MS/MS. The extraction and clean-up can process up to 24 samples in series within 4 hours. The time required for dilution, evaporation, and filtration of the final extracts prior to LC/MS/MS analysis was approximately 3 hours. The sample to sample LC/MS/MS analysis time was 23 minutes.

5.3 ***Modifications or Special Precautions***

Due to the broad range of residues fortified and potentially found in treated samples (0.05 to 0.5 µg/L), special precautions should be taken to insure reusable labware is clean, test materials are handled to minimize cross-contamination, and instrument (LC-MS/MS) are maintained to avoid carryover or contamination that can affect method performance.

5.4 Method Ruggedness

5.4.1 *Stability*

All stock and standard solutions prepared in methanol and stored at 4-8°C are stable for at least two months.

5.4.2 *Specificity/Potential Interference*

5.4.2.a *Interference from Glassware & Reagents, Matrices*

No interferences attributable to glassware, reagents, or matrices were observed to co-elute with test analytes.

5.4.2.b *Interference from Other Pesticides*

Due to the highly specific and selective nature of detection by LC/MS/MS of this method (two individual molecular ion transitions monitored), interference peaks were not observed at the retention time of the analytes. As a result of the highly specific detection used, interference testing is not necessary for this method.

5.4.3 *Confirmatory Procedure*

Two independent MS/MS transitions of the molecular ion for each analyte were monitored. The relative response ratios of the two fragment ions (base peak/secondary peak) were determined from calibration standard responses for confirmation of analyte in water matrix samples. Acceptable confirmation criteria are a co-eluting peak and equivalent ion ratio, each within ± 30% of the average response observed in calibration standards at or above the LOQ equivalent concentration concurrently analyzed with the samples. The calculated response ratios for each analyte determined in an analysis set are shown in Table 13.

6.0 CONCLUSIONS

- This analytical method is suitable for the quantitation of diuron, linuron, DCPMU, DCPU, mCPDMU and desmethylated linuron residues in water matrices. The results support an LOQ of 0.05 µg/L and an estimated LOD of 0.01 µg/L in water. The method meets European Commission, Directorate General Health and Consumer Protection. "Guidance Document on Residue Analytical Methods", SANCO/825/00 rev. 7, March 17, 2004.
- The overall average recoveries for each analyte and matrix in the validation trials ranged from 86% (mCPDMU in surface water) to 103% (desmethylated linuron, in drinking water) with maximum RSD of 8%.
- Residue confirmation for each analyte was demonstrated at 0.05 µg/L (LOQ) and 0.5 µg/L fortification levels based on retention time and the relative ratios of two MS/MS parent-to-fragment ion transitions detected during sample analysis.

7.0 RETENTION OF RECORDS

Originals or exact copies of all raw data and pertinent information and the final report will be retained at:

E. I. du Pont de Nemours and Company
DuPont Crop Protection
Global Technology Division
Stine-Haskell GmbH Center
Newark, Delaware 19714-0030

Archiving at SGS INSTITUT FRESENIUS

Documents

SGS INSTITUT FRESENIUS GmbH will archive the following documents under GLP-conditions:

- certified copies of the study plan and additional amendments, if any
- the certified copies raw data
- a certified copy of the report

Materials

- Reference items

A specimen of the reference items will be archived for a period of time specified in German GLP-regulations. After this period, the specimen will be disposed of in the correct way.

- Specimens

All specimen materials used in this study will be stored until the date of the report.

TABLE 1 VALIDATION DRINKING WATER - RECOVERY RESULTS FOR DIURON

Validated matrix: Drinking water
Date of extraction: June 23, 2006
Date of analysis: June 23, 2006

Analyte (transition)			Quantification Diuron (233 ≥ 72)		Confirmation Diuron (233 ≥ 46)	
SGS IF specimen code	Specimen weight (g)	Fortication level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202451-1	20.04	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-2	20.03	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-A	20.03	0.0502	0.0483	96	0.0448	89
010/6202451-B	20.04	0.0501	0.0471	94	0.0430	86
010/6202451-C	20.02	0.0502	0.0531	106	0.0493	98
010/6202451-D	20.02	0.0502	0.0477	95	0.0465	93
010/6202451-E	20.04	0.0501	0.0540	108	0.0470	94
Number				5		5
Mean recovery (%)				100		92
RSD (%)				7		5
010/6202451-F	20.07	0.5007	0.4994	100	0.4732	94
010/6202451-G	20.05	0.5012	0.4581	91	0.4859	97
010/6202451-H	20.04	0.5015	0.5469	109	0.4742	95
010/6202451-K	20.01	0.5022	0.5200	104	0.4394	87
010/6202451-L	20.09	0.5002	0.4855	97	0.4217	84
Number				5		5
Mean recovery (%)				100		92
RSD (%)				7		6
Number				10		10
Mean recovery (%)				100		92
RSD (%)				6		5

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 2 VALIDATION DRINKING WATER - RECOVERY RESULTS FOR LINURON

Validated matrix: Drinking water
Date of extraction: June 23, 2006
Date of analysis: June 23, 2006

Analyte (transition)			Quantification Linuron (249 ≥ 60)		Confirmation Linuron (249 ≥ 82)	
SGS IF specimen code	Specimen weight (g)	Fortication level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202451-1	20.04	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-2	20.03	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-A	20.03	0.0505	0.0428	85	0.0477	94
010/6202451-B	20.04	0.0505	0.0450	89	0.0543	107
010/6202451-C	20.02	0.0505	0.0425	84	0.0461	91
010/6202451-D	20.02	0.0505	0.0456	90	0.0505	100
010/6202451-E	20.04	0.0505	0.0469	93	0.0516	102
Number				5		5
Mean recovery (%)				88		99
RSD (%)				4		6
010/6202451-F	20.07	0.5042	0.4915	97	0.5501	109
010/6202451-G	20.05	0.5047	0.4540	90	0.4882	97
010/6202451-H	20.04	0.5050	0.5072	100	0.5516	109
010/6202451-K	20.01	0.5057	0.4792	95	0.5462	108
010/6202451-L	20.09	0.5037	0.4534	90	0.5011	99
Number				5		5
Mean recovery (%)				95		105
RSD (%)				5		6
Number				10		10
Mean recovery (%)				91		102
RSD (%)				6		6

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 3 VALIDATION DRINKING WATER - RECOVERY RESULTS FOR DCPMU

Validated matrix: Drinking water
Date of extraction: June 23, 2006
Date of analysis: June 23, 2006

Analyte (transition)			Quantification DCPMU (219 ≥ 27)		Confirmation DCPMU (219 ≥ 62)	
SGS IF specimen code	Specimen weight (g)	Fortication level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202451-1	20.04	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-2	20.03	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-A	20.03	0.0503	0.0439	87	0.0454	90
010/6202451-B	20.04	0.0502	0.0477	95	0.0456	91
010/6202451-C	20.02	0.0503	0.0429	85	0.0452	90
010/6202451-D	20.02	0.0503	0.0458	91	0.0477	95
010/6202451-E	20.04	0.0502	0.0487	97	0.0526	105
Number				5		5
Mean recovery (%)				91		94
RSD (%)				5		7
010/6202451-F	20.07	0.5017	0.4800	96	0.5096	102
010/6202451-G	20.05	0.5022	0.4451	89	0.4701	94
010/6202451-H	20.04	0.5025	0.4900	98	0.5458	109
010/6202451-K	20.01	0.5032	0.5019	100	0.5539	110
010/6202451-L	20.09	0.5012	0.4715	94	0.5412	108
Number				5		5
Mean recovery (%)				95		104
RSD (%)				4		7
Number				10		10
Mean recovery (%)				93		99
RSD (%)				5		8

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 4 VALIDATION DRINKING WATER - RECOVERY RESULTS FOR DCPU

Validated matrix: Drinking water
Date of extraction: June 23, 2006
Date of analysis: June 23, 2006

Analyte (transition)		Quantification DCPU (205 ≥ 27)			Confirmation DCPU (205 ≥ 62)	
SGS IF specimen code	Specimen weight (g)	Fortication level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202451-1	20.04	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-2	20.03	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-A	20.03	0.0504	0.0412	82	0.0415	82
010/6202451-B	20.04	0.0504	0.0412	82	0.0399	79
010/6202451-C	20.02	0.0504	0.0412	82	0.0403	80
010/6202451-D	20.02	0.0504	0.0419	83	0.0404	80
010/6202451-E	20.04	0.0504	0.0467	93	0.0417	83
Number				5		5
Mean recovery (%)				84		81
RSD (%)				6		2
010/6202451-F	20.07	0.5032	0.4553	90	0.4997	99
010/6202451-G	20.05	0.5037	0.4603	91	0.4059	81
010/6202451-H	20.04	0.5040	0.4863	96	0.5058	100
010/6202451-K	20.01	0.5047	0.5275	105	0.4589	91
010/6202451-L	20.09	0.5027	0.4631	92	0.4628	92
Number				5		5
Mean recovery (%)				95		93
RSD (%)				6		9
Number				10		10
Mean recovery (%)				90		87
RSD (%)				8		9

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 5 VALIDATION DRINKING WATER - RECOVERY RESULTS FOR DESM - LINURON

Validated matrix: Drinking water
Date of extraction: June 23, 2006
Date of analysis: June 23, 2006

Analyte (transition)			Quantification desm. Linuron (235 ≥ 60)		Confirmation desm. Linuron (235 ≥ 61)	
SGS IF specimen code	Specimen weight (g)	Fortication level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202451-1	20.04	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-2	20.03	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-A	20.03	0.0503	0.0520	103	0.0519	103
010/6202451-B	20.04	0.0502	0.0495	98	0.0547	109
010/6202451-C	20.02	0.0503	0.0468	93	0.0494	98
010/6202451-D	20.02	0.0503	0.0534	106	0.0511	102
010/6202451-E	20.04	0.0502	0.0524	104	0.0533	106
Number				5		5
Mean recovery (%)				101		104
RSD (%)				5		4
010/6202451-F	20.07	0.5017	0.5326	106	0.5047	101
010/6202451-G	20.05	0.5022	0.4937	98	0.5214	104
010/6202451-H	20.04	0.5025	0.5966	119	0.5350	106
010/6202451-K	20.01	0.5032	0.5440	108	0.5568	111
010/6202451-L	20.09	0.5012	0.4764	95	0.5283	105
Number				5		5
Mean recovery (%)				105		105
RSD (%)				9		3
Number				10		10
Mean recovery (%)				103		104
RSD (%)				7		4

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 6 VALIDATION DRINKING WATER - RECOVERY RESULTS FOR MCPDMU

Validated matrix: Drinking water
Date of extraction: June 23, 2006
Date of analysis: June 23, 2006

Analyte (transition)			Quantification mCPDMU (199 ≥ 72)		Confirmation mCPDMU (199 ≥ 46)	
SGS IF specimen code	Specimen weight (g)	Fortication level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202451-1	20.04	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-2	20.03	-	< 0.05 nd	-	< 0.05 nd	-
010/6202451-A	20.03	0.0506	0.0493	97	0.0403	80
010/6202451-B	20.04	0.0506	0.0474	94	0.0460	91
010/6202451-C	20.02	0.0506	0.0469	93	0.0448	88
010/6202451-D	20.02	0.0506	0.0456	90	0.0418	83
010/6202451-E	20.04	0.0506	0.0537	106	0.0431	85
Number				5		5
Mean recovery (%)				96		85
RSD (%)				7		5
010/6202451-F	20.07	0.5052	0.5220	103	0.4725	94
010/6202451-G	20.05	0.5057	0.4585	91	0.4526	89
010/6202451-H	20.04	0.5060	0.5311	105	0.5331	105
010/6202451-K	20.01	0.5067	0.5571	110	0.5528	109
010/6202451-L	20.09	0.5047	0.5153	102	0.4743	94
Number				5		5
Mean recovery (%)				102		98
RSD (%)				7		9
Number				10		10
Mean recovery (%)				99		92
RSD (%)				7		10

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 7 VALIDATION SURFACE WATER - RECOVERY RESULTS FOR DIURON

Validated matrix: Surface water
Date of extraction: June 22, 2006
Date of analysis: June 22, 2006

Analyte (transition)		Quantification Diuron (233 ≥ 72)			Confirmation Diuron (233 ≥ 46)	
SGS IF specimen code	Specimen weight (g)	Fortification level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202452-1	20.01	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-2	20.06	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-A	20.02	0.0502	0.0535	107	0.0528	105
010/6202452-B	20.03	0.0502	0.0485	97	0.0503	100
010/6202452-C	20.07	0.0501	0.0459	92	0.0523	105
010/6202452-D	20.05	0.0501	0.0524	104	0.0489	98
010/6202452-E	20.01	0.0502	0.0490	98	0.0484	96
Number				5		5
Mean recovery (%)				99		101
RSD (%)				6		4
010/6202452-F	20.06	0.5010	0.4636	93	0.5088	102
010/6202452-G	20.06	0.5010	0.5129	102	0.4721	94
010/6202452-H	20.05	0.5012	0.4740	95	0.4776	95
010/6202452-K	20.00	0.5025	0.5280	105	0.5229	104
010/6202452-L	20.02	0.5020	0.5186	103	0.4917	98
Number				5		5
Mean recovery (%)				100		99
RSD (%)				6		4
Number				10		10
Mean recovery (%)				99		100
RSD (%)				6		4

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 8 VALIDATION SURFACE WATER - RECOVERY RESULTS FOR LINURON

Validated matrix: Surface water
Date of extraction: June 22, 2006
Date of analysis: June 22, 2006

Analyte (transition)			Quantification Linuron (249 ≥ 160)		Confirmation Linuron (249 ≥ 182)	
SGS IF specimen code	Specimen weight (g)	Fortification level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202452-1	20.01	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-2	20.06	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-A	20.02	0.0505	0.0487	96	0.0527	104
010/6202452-B	20.03	0.0505	0.0464	92	0.0467	92
010/6202452-C	20.07	0.0504	0.0410	81	0.0486	96
010/6202452-D	20.05	0.0505	0.0446	88	0.0442	88
010/6202452-E	20.01	0.0506	0.0420	83	0.0447	88
Number				5		5
Mean recovery (%)				88		94
RSD (%)				7		7
010/6202452-F	20.06	0.5045	0.4703	93	0.4329	86
010/6202452-G	20.06	0.5045	0.4276	85	0.4203	83
010/6202452-H	20.05	0.5047	0.4203	83	0.4096	81
010/6202452-K	20.00	0.5060	0.4527	89	0.4328	86
010/6202452-L	20.02	0.5055	0.4438	88	0.4407	87
Number				5		5
Mean recovery (%)				88		85
RSD (%)				4		3
Number				10		10
Mean recovery (%)				88		89
RSD (%)				6		8

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 9 VALIDATION SURFACE WATER - RECOVERY RESULTS FOR DCPMU

Validated matrix: Surface water
Date of extraction: June 22, 2006
Date of analysis: June 22, 2006

Analyte (transition)			Quantification DCPMU (219 ≥ 127)		Confirmation DCPMU (219 ≥ 162)	
SGS IF specimen code	Specimen weight (g)	Fortification level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202452-1	20.01	-	< 0.05	-	< 0.05	-
010/6202452-2	20.06	-	< 0.05	-	< 0.05	-
010/6202452-A	20.02	0.0503	0.0506	101	0.0498	99
010/6202452-B	20.03	0.0503	0.0450	90	0.0497	99
010/6202452-C	20.07	0.0502	0.0425	85	0.0474	94
010/6202452-D	20.05	0.0502	0.0451	90	0.0490	98
010/6202452-E	20.01	0.0503	0.0449	89	0.0537	107
Number				5		5
Mean recovery (%)				91		99
RSD (%)				7		5
010/6202452-F	20.06	0.5020	0.4482	89	0.4581	91
010/6202452-G	20.06	0.5020	0.4731	94	0.5098	102
010/6202452-H	20.05	0.5022	0.4570	91	0.4707	94
010/6202452-K	20.00	0.5035	0.4675	93	0.5253	104
010/6202452-L	20.02	0.5030	0.4902	97	0.5320	106
Number				5		5
Mean recovery (%)				93		99
RSD (%)				3		7
Number				10		10
Mean recovery (%)				92		99
RSD (%)				5		5

RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 10 VALIDATION SURFACE WATER - RECOVERY RESULTS FOR DCPU

Validated matrix: Surface water
Date of extraction: June 22, 2006
Date of analysis: June 22, 2006

Analyte (transition)			Quantification DCPU (205 ≥ 127)		Confirmation DCPU (205 ≥ 162)	
SGS IF specimen code	Specimen weight (g)	Fortification level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202452-1	20.01	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-2	20.06	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-A	20.02	0.0504	0.0529	105	0.0542	107
010/6202452-B	20.03	0.0504	0.0462	92	0.0547	108
010/6202452-C	20.07	0.0503	0.0456	91	0.0489	97
010/6202452-D	20.05	0.0504	0.0531	105	0.0483	96
010/6202452-E	20.01	0.0505	0.0475	94	0.0487	97
Number				5		5
Mean recovery (%)				97		101
RSD (%)				7		6
010/6202452-F	20.06	0.5035	0.4374	87	0.4441	88
010/6202452-G	20.06	0.5035	0.5019	100	0.5431	108
010/6202452-H	20.05	0.5037	0.4424	88	0.4617	92
010/6202452-K	20.00	0.5050	0.5128	102	0.5497	109
010/6202452-L	20.02	0.5045	0.4886	97	0.5085	101
Number				5		5
Mean recovery (%)				95		99
RSD (%)				7		9
Number				10		10
Mean recovery (%)				96		100
RSD (%)				7		8

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 11 VALIDATION SURFACE WATER - RECOVERY RESULTS FOR DESM. LINURON

Validated matrix: Surface water
Date of extraction: June 22, 2006
Date of analysis: June 22, 2006

Analyte (transition)			Quantification desm. Linuron (235 ≥ 160)		Confirmation desm. Linuron (235 ≥ 161)	
SGS IF specimen code	Specimen weight (g)	Fortification level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202452-1	20.01	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-2	20.06	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-A	20.02	0.0503	0.0492	98	0.0451	90
010/6202452-B	20.03	0.0503	0.0518	103	0.0511	102
010/6202452-C	20.07	0.0502	0.0484	97	0.0515	103
010/6202452-D	20.05	0.0502	0.0479	95	0.0535	106
010/6202452-E	20.01	0.0503	0.0415	82	0.0514	102
Number				5		5
Mean recovery (%)				95		101
RSD (%)				8		6
010/6202452-F	20.06	0.5020	0.4604	92	0.5060	101
010/6202452-G	20.06	0.5020	0.4461	89	0.4010	80
010/6202452-H	20.05	0.5022	0.4492	89	0.4512	90
010/6202452-K	20.00	0.5035	0.4510	90	0.4293	85
010/6202452-L	20.02	0.5030	0.4322	86	0.4029	80
Number				5		5
Mean recovery (%)				89		87
RSD (%)				2		10
Number				10		10
Mean recovery (%)				92		94
RSD (%)				7		11

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 12 VALIDATION SURFACE WATER - RECOVERY RESULTS FOR MCPDMU

Validated matrix: Surface water
Date of extraction: June 22, 2006
Date of analysis: June 22, 2006

Analyte (transition)			Quantification mCPDMU (199 ≥ 72)		Confirmation mCPDMU (199 ≥ 46)	
SGS IF specimen code	Specimen weight (g)	Fortification level (µg/L)	Found (µg/L)	Recovery rate (%)	Found (µg/L)	Recovery rate (%)
010/6202452-1	20.01	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-2	20.06	-	< 0.05 nd	-	< 0.05 nd	-
010/6202452-A	20.02	0.0506	0.0483	95	0.0521	103
010/6202452-B	20.03	0.0506	0.0455	90	0.0430	85
010/6202452-C	20.07	0.0505	0.0414	82	0.0439	87
010/6202452-D	20.05	0.0506	0.0447	88	0.0473	93
010/6202452-E	20.01	0.0507	0.0456	90	0.0471	93
Number				5		5
Mean recovery (%)				89		92
RSD (%)				5		8
010/6202452-F	20.06	0.5055	0.4347	86	0.4241	84
010/6202452-G	20.06	0.5055	0.4144	82	0.4163	82
010/6202452-H	20.05	0.5057	0.4129	82	0.4312	85
010/6202452-K	20.00	0.5070	0.4159	82	0.4318	85
010/6202452-L	20.02	0.5065	0.4388	87	0.4608	91
Number				5		5
Mean recovery (%)				84		86
RSD (%)				3		4
Number				10		10
Mean recovery (%)				86		89
RSD (%)				5		7

nd: no peak detected
RSD: relative standard deviation

The tabulated values are rounded values, calculated on basis of the exact results.

TABLE 13 CONFIRMATION- RATIO TRANSITION FOR QUANTIFICATION TO TRANSITION FOR CONFIRMATION

Standard solution 1-ng/mL series drinking water

	Transition quantification	Area - peak for quantification	Transition confirmation	Area - peak for confirmation	Peak ratio
Diuron	233 ≥ 72	22872	233 ≥ 46	5096	4.5
Linuron	249 ≥ 160	17839	249 ≥ 182	15300	1.2
DCPMU	219 ≥ 127	21315	219 ≥ 162	16666	1.3
DCPU	205 ≥ 127	10331	205 ≥ 162	5208	2.0
Desm. Linuron	235 ≥ 160	6750	235 ≥ 161	5223	1.3
mCPDMU	199 ≥ 72	49417	199 ≥ 46	11580	4.3

Standard solution 1-ng/mL series surface water

	Transition quantification	Area - peak for quantification	Transition confirmation	Area - peak for confirmation	Peak ratio
Diuron	233 ≥ 72	21825	233 ≥ 46	3998	5.5
Linuron	249 ≥ 160	15861	249 ≥ 182	13802	1.1
DCPMU	219 ≥ 127	17463	219 ≥ 162	14569	1.2
DCPU	205 ≥ 127	9582	205 ≥ 162	5073	1.9
Desm. Linuron	235 ≥ 160	6611	235 ≥ 161	5351	1.2
mCPDMU	199 ≥ 72	44936	199 ≥ 46	8994	5.0

FIGURE 1 REPRESENTATIVE DIURON MASS SPECTRA

LC/MS/MS Full Scan Mass Spectrum

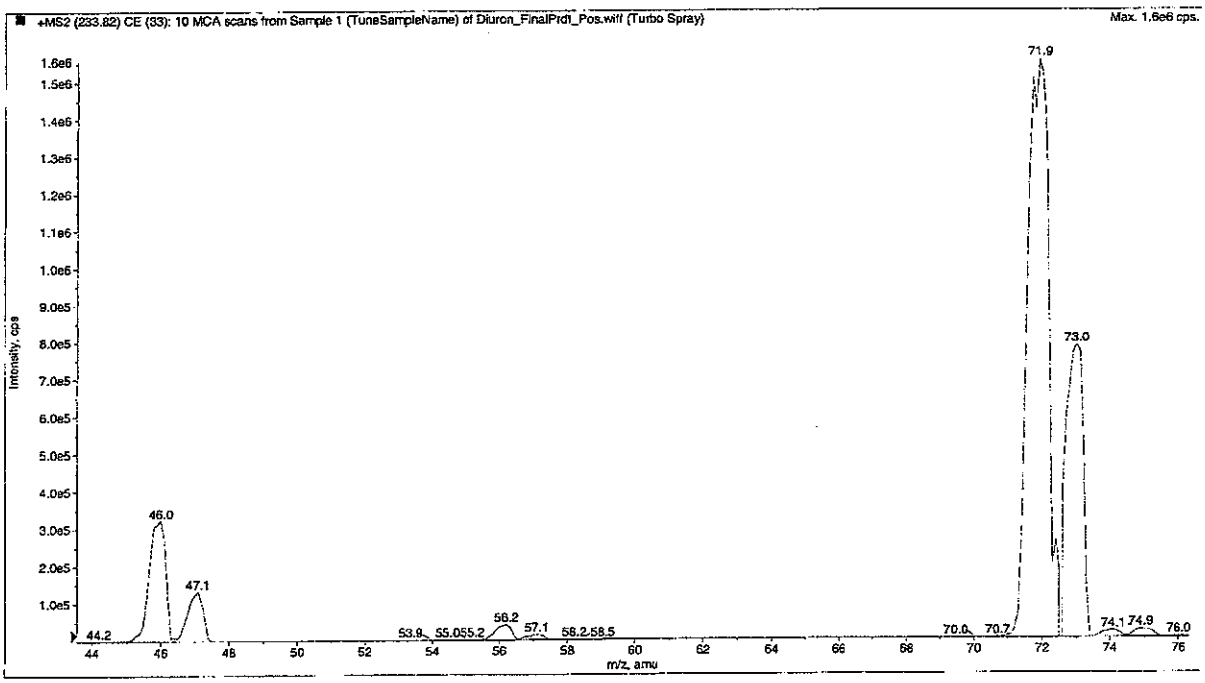


FIGURE 2 REPRESENTATIVE LINURON MASS SPECTRA

LC/MS/MS Full Scan Mass Spectrum

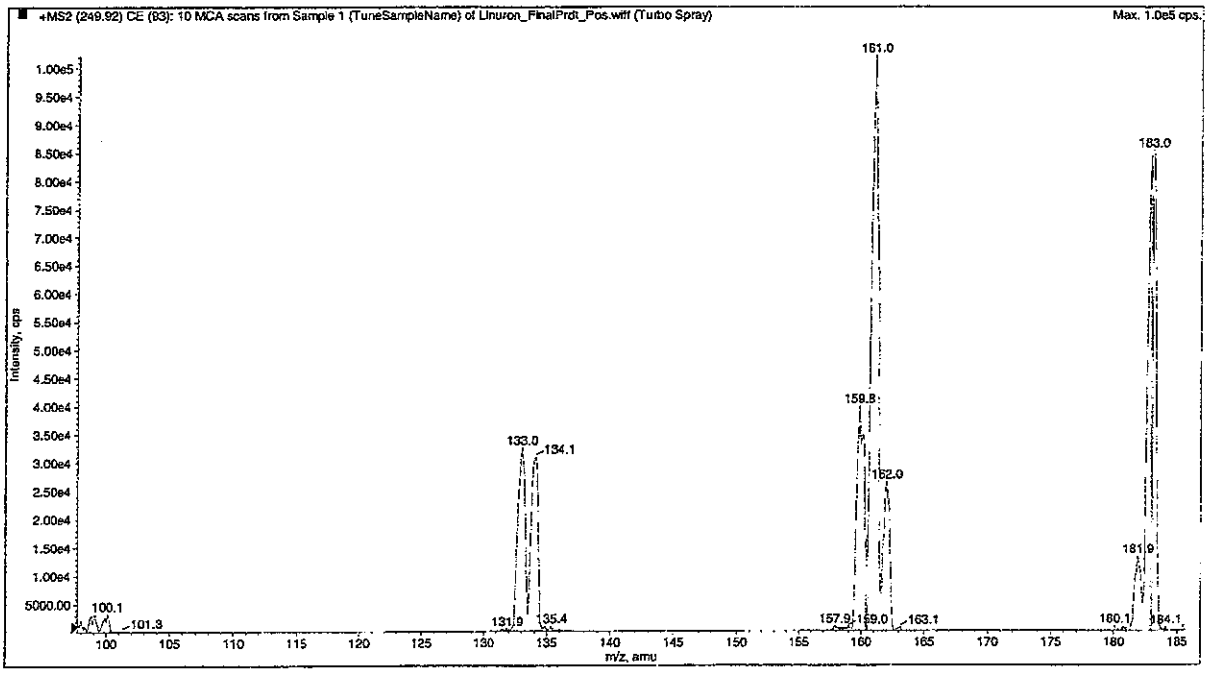


FIGURE 3 REPRESENTATIVE DCPMU MASS SPECTRA

LC/MS/MS Full Scan Mass Spectrum

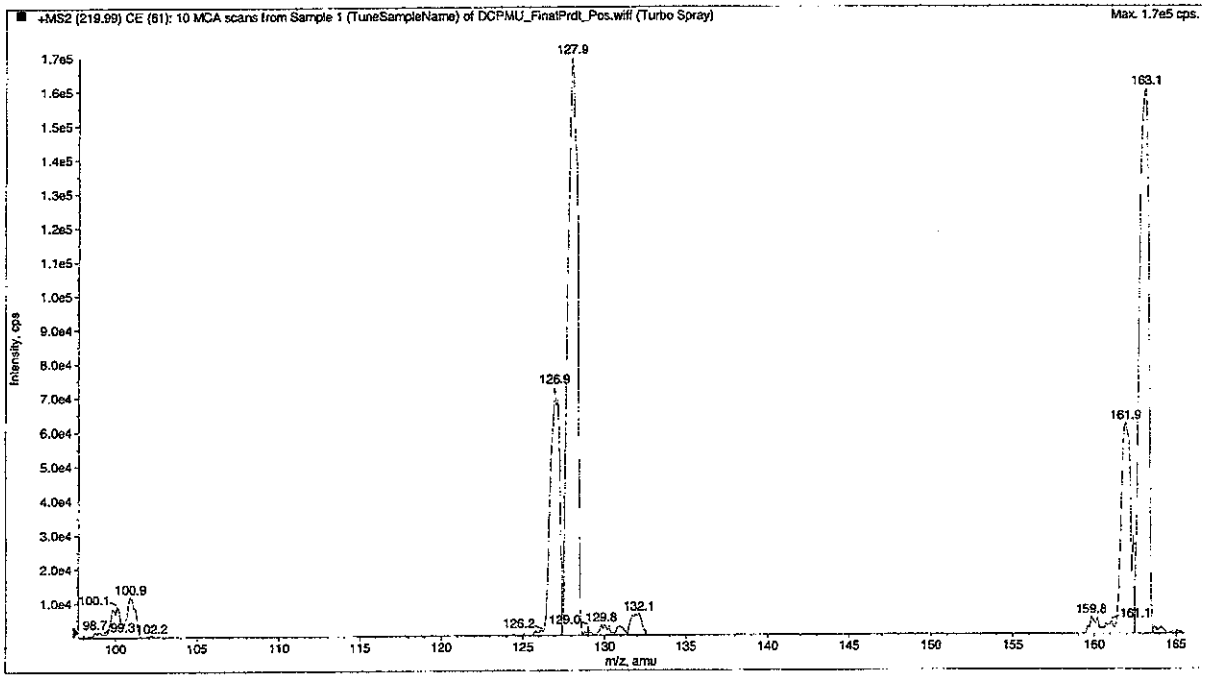


FIGURE 4 REPRESENTATIVE DCPU MASS SPECTRA

LC/MS/MS Full Scan Mass Spectrum

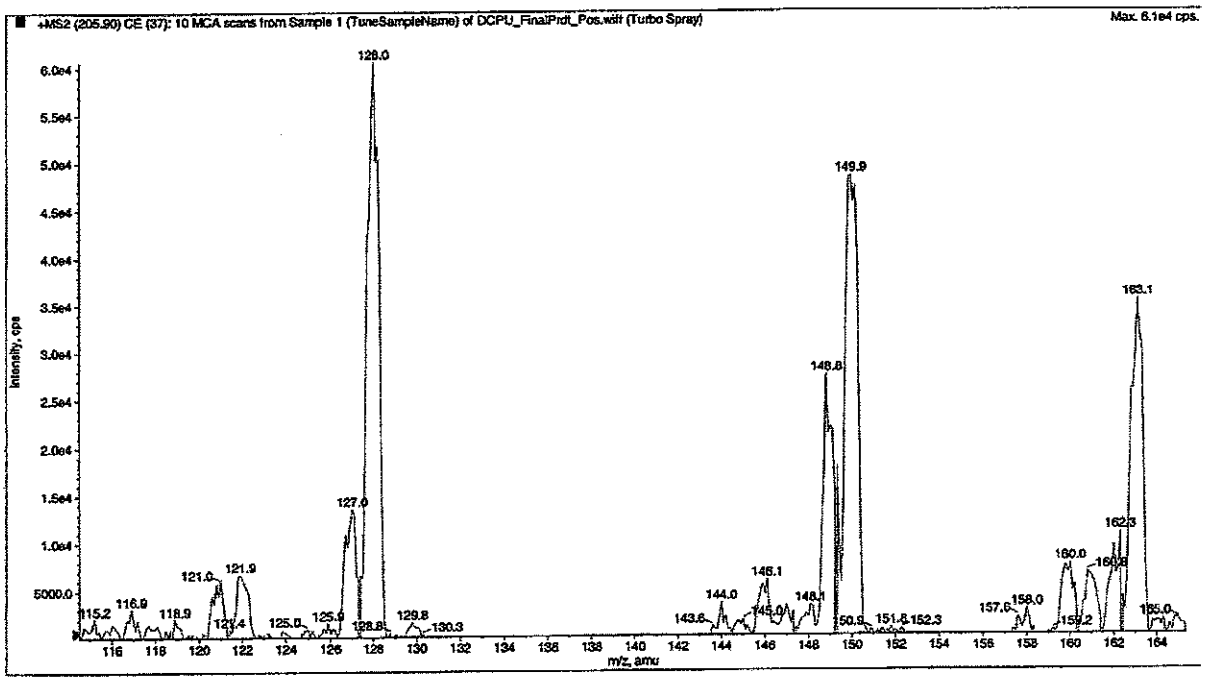


FIGURE 5 REPRESENTATIVE MCPDMU MASS SPECTRA

LC/MS/MS Full Scan Mass Spectrum

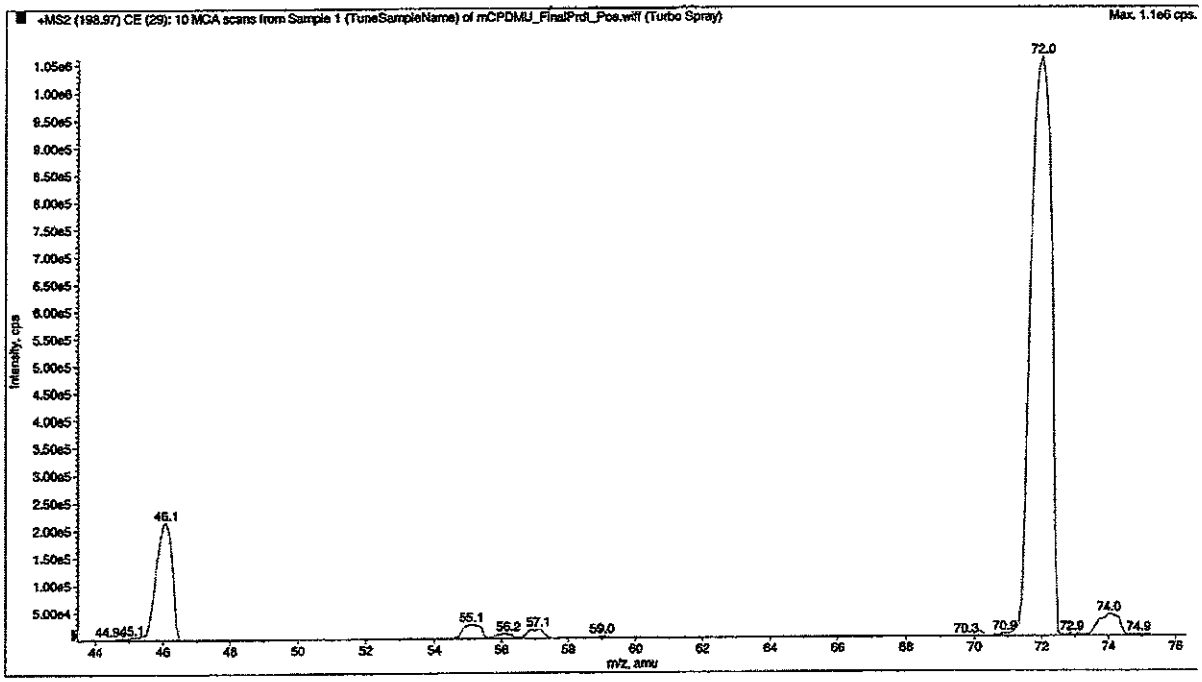


FIGURE 6 REPRESENTATIVE DESMETHYLATED LINURON MASS SPECTRA

LC/MS/MS Full Scan Mass Spectrum

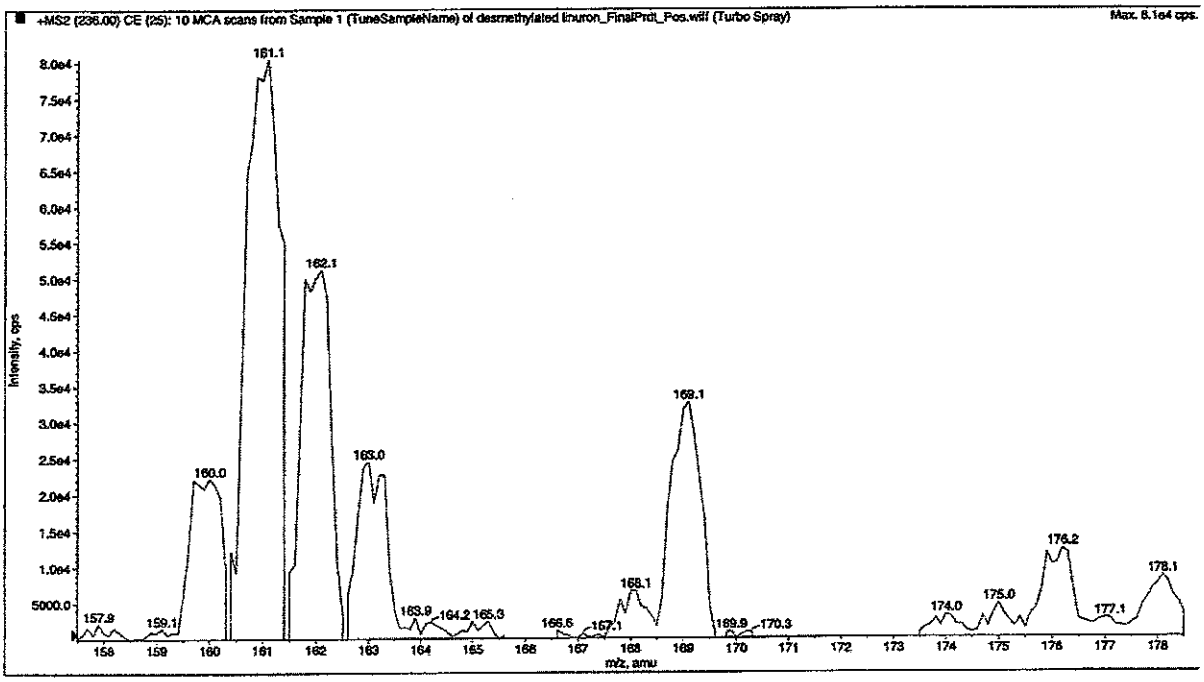
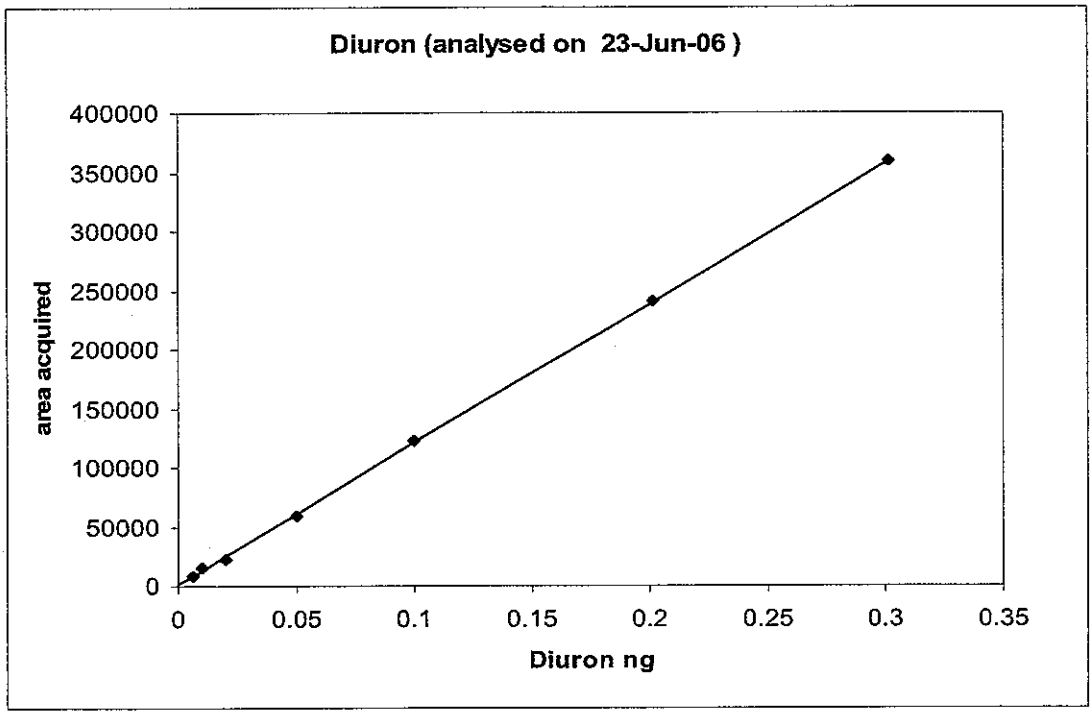
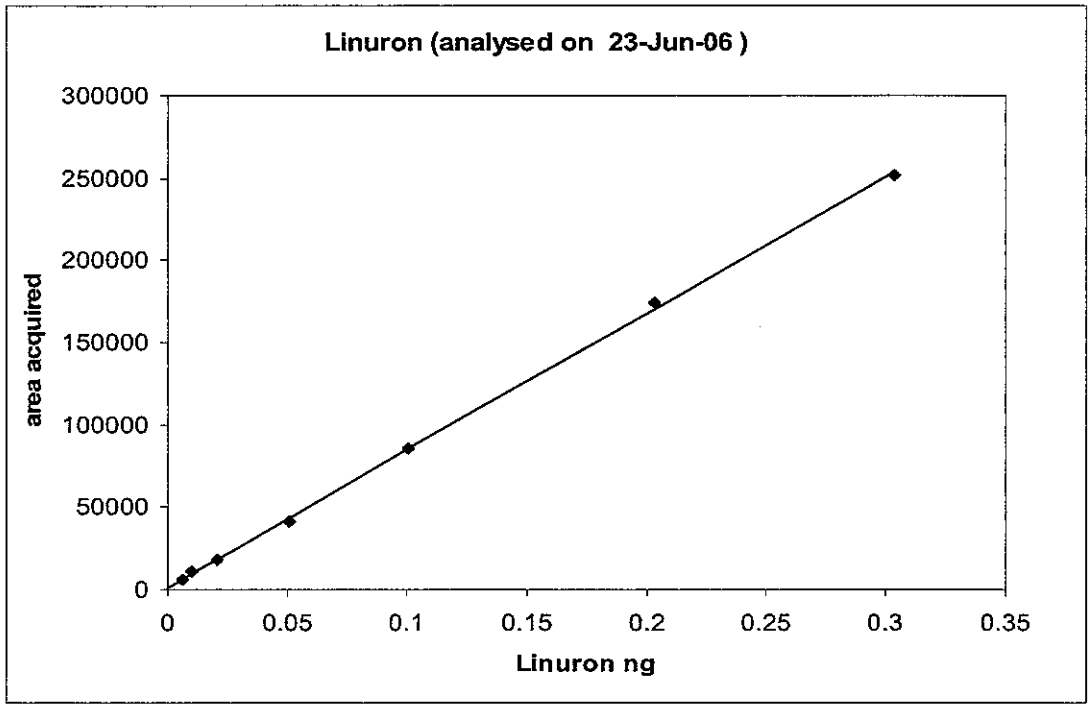


FIGURE 7 REPRESENTATIVE CALIBRATION CURVE - DIURON



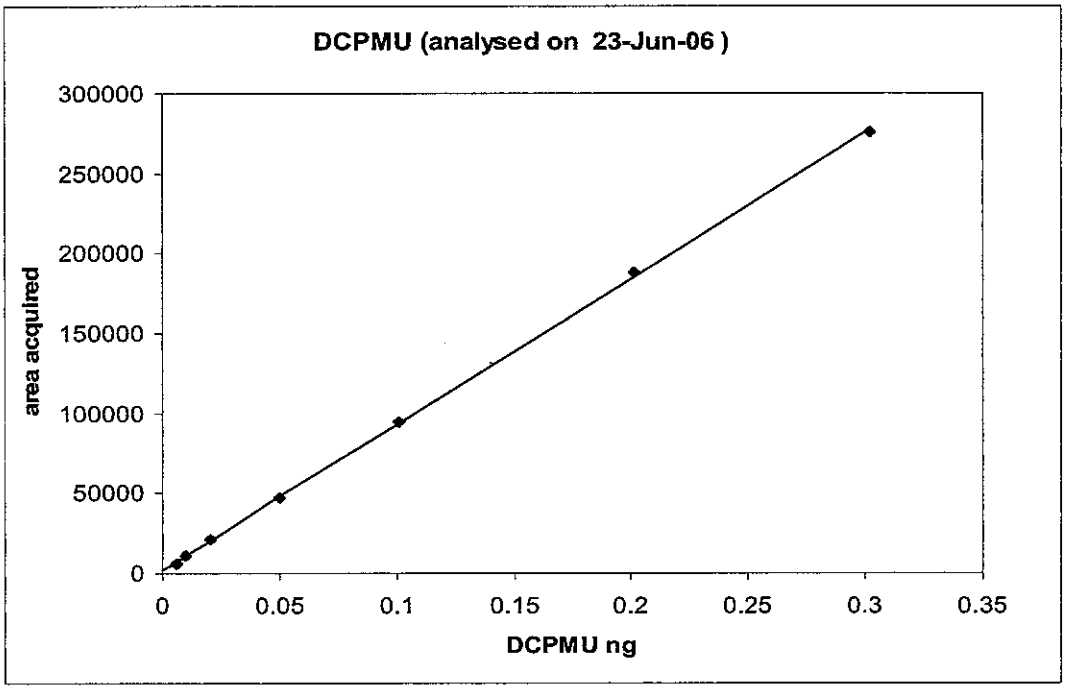
y = a + bx
a = 1100
b = 1188649.98
R = 0.99989

FIGURE 8 REPRESENTATIVE CALIBRATION CURVE – LINURON



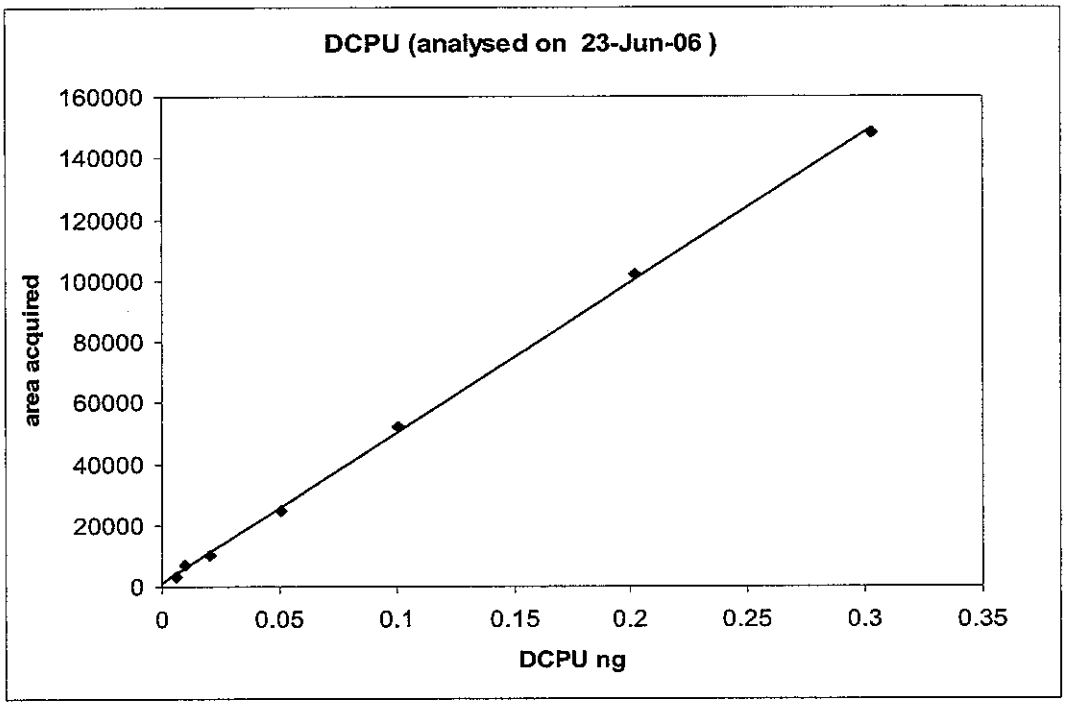
y = a + bx
a = 1474
b = 830932.4
R = 0.99974

FIGURE 9 REPRESENTATIVE CALIBRATION CURVE – DCPMU



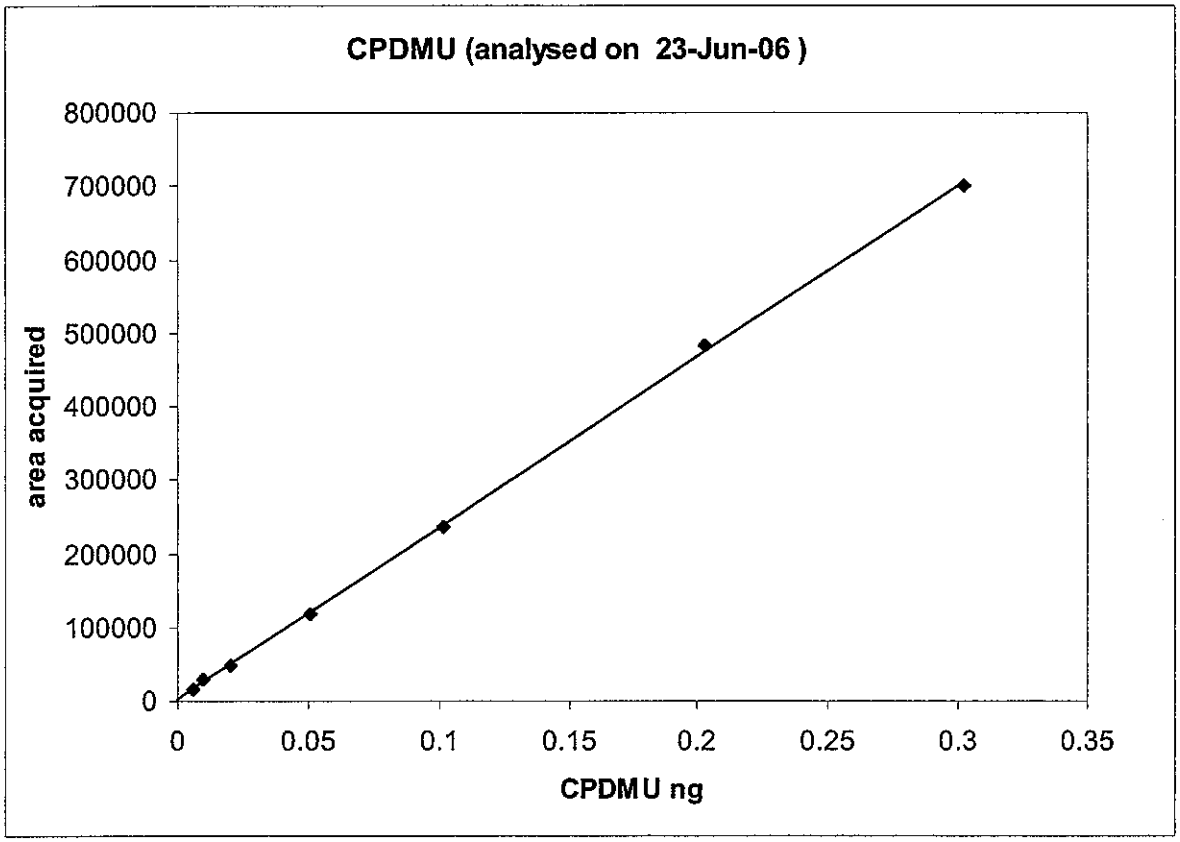
y = a + bx
a = 2008
b = 912005.8
R = 0.99992

FIGURE 10 REPRESENTATIVE CALIBRATION CURVE – DCPU



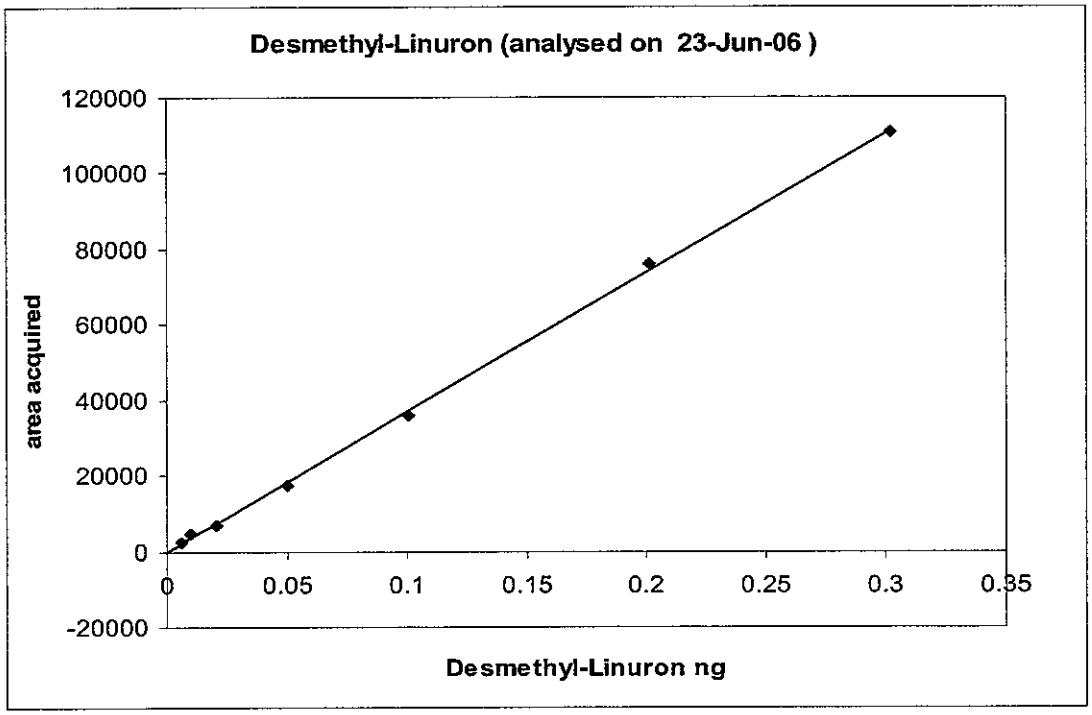
y = a + bx
a = 1175
b = 490218.3
R = 0.99969

FIGURE 11 REPRESENTATIVE CALIBRATION CURVE – MCPDMU



y =a + bx
a = 3355
b = 2324106.51
R = 0.99986

FIGURE 12 REPRESENTATIVE CALIBRATION CURVE – DESMETHLYL - LINURON



y = a + bx
a = -108.1
b = 368702
R = 0.99968

FIGURE 13 DRINKING WATER – DIURON – STANDARD SOLUTION 1 NG/ML

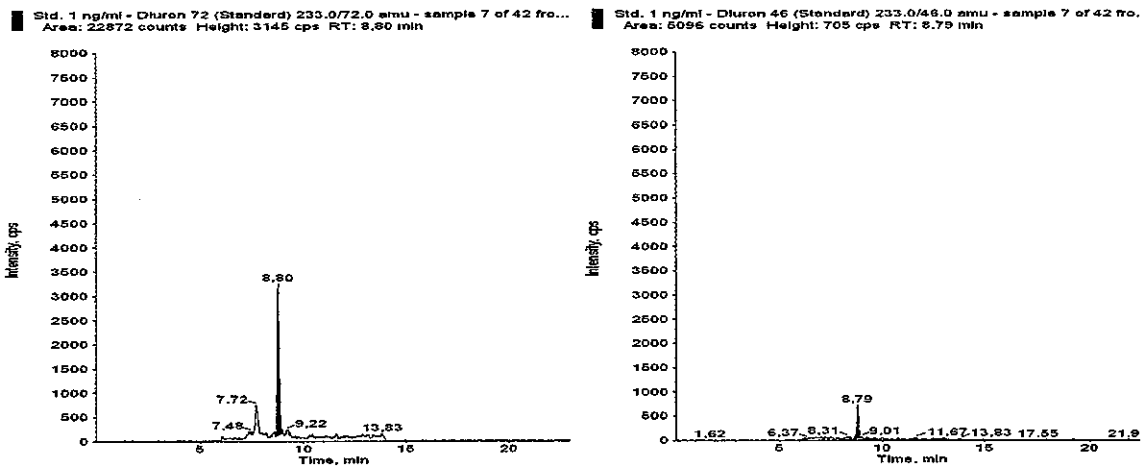


FIGURE 14 DRINKING WATER – LINURON – STANDARD SOLUTION 1 NG/ML

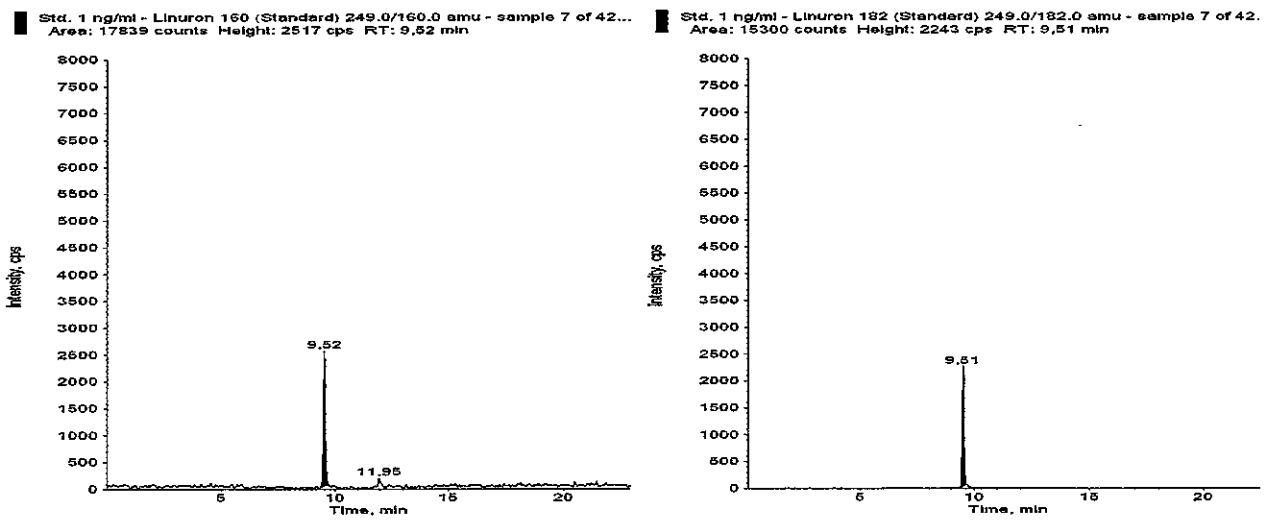


FIGURE 15 DRINKING WATER – DCPMU – STANDARD SOLUTION 1 NG/ML

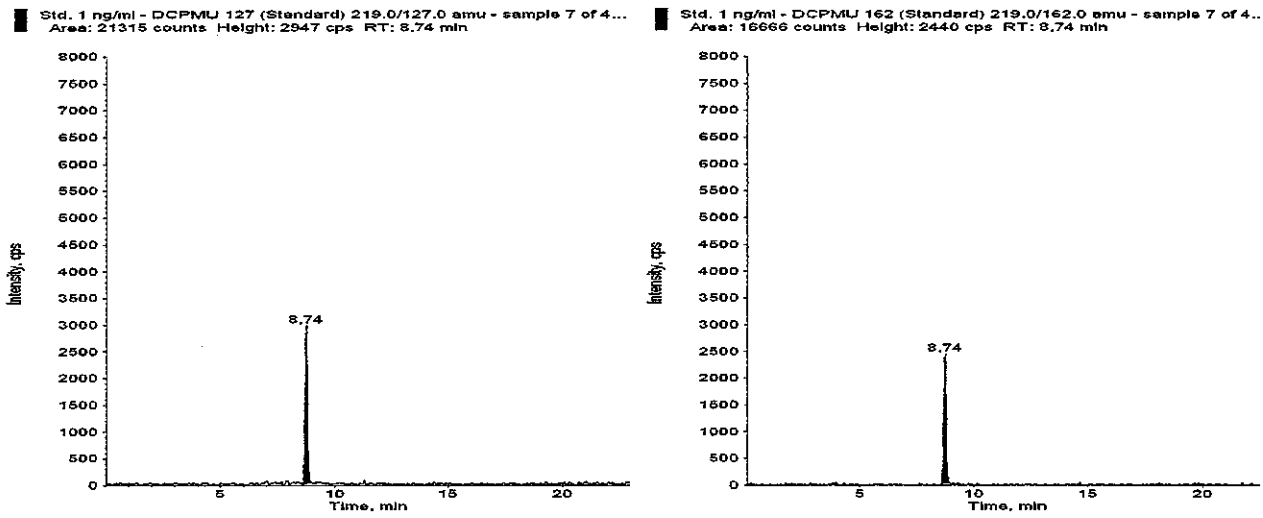


FIGURE 16 DRINKING WATER – DCPU – STANDARD SOLUTION 1 NG/ML

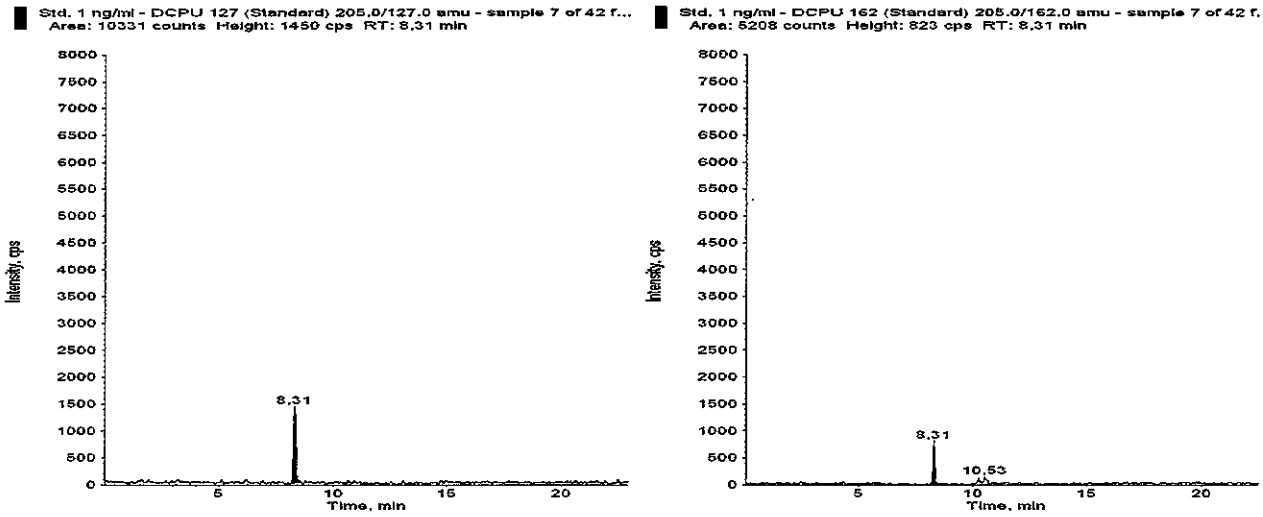


FIGURE 17 DRINKING WATER – DES. LINURON – STANDARD SOLUTION 1 NG/ML

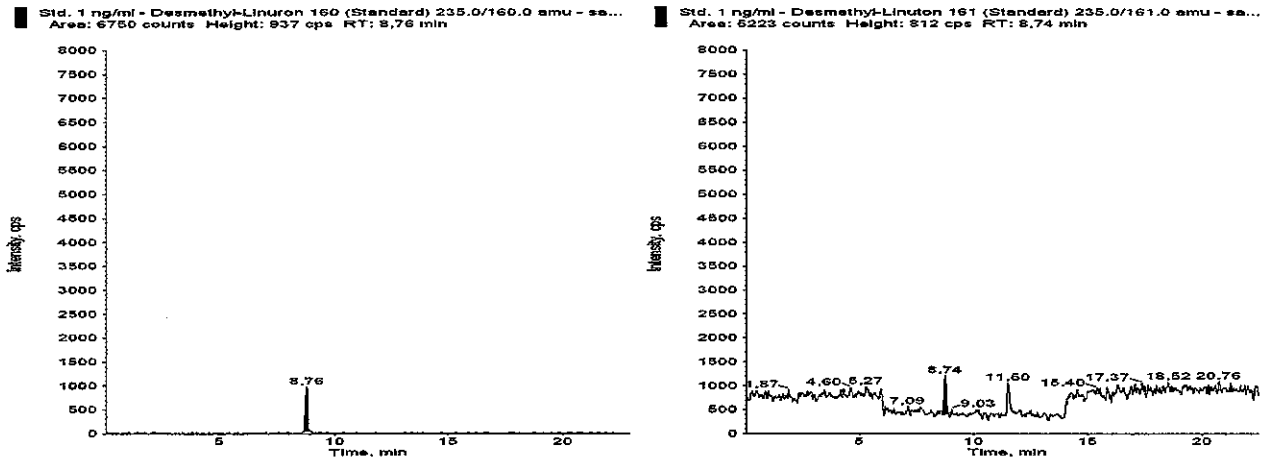


FIGURE 18 DRINKING WATER – MCPDMU – STANDARD SOLUTION 1 NG/ML

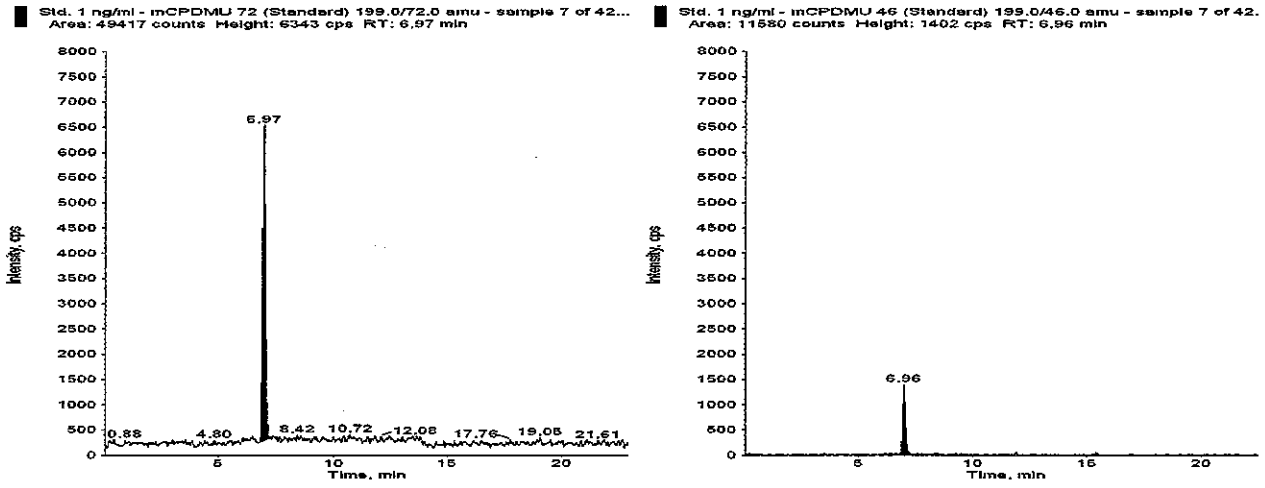


FIGURE 19 DRINKING WATER – DIURON – BLANK VALUE, NO PEAK FOUND

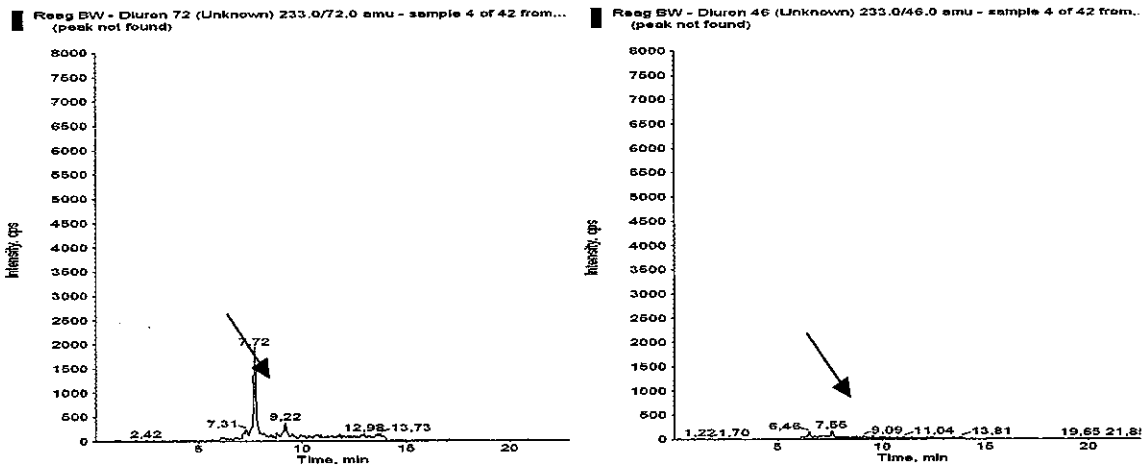


FIGURE 20 DRINKING WATER – LINURON – BLANK VALUE, NO PEAK FOUND

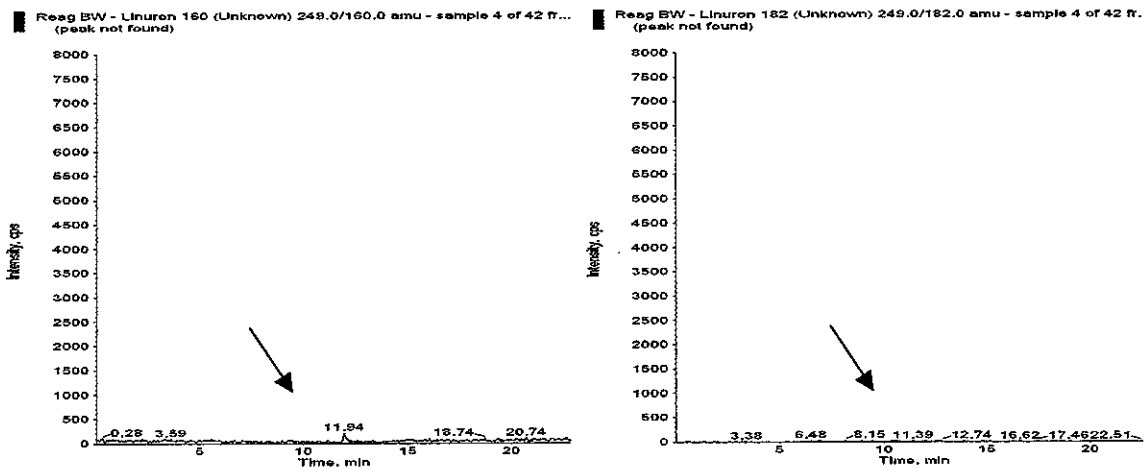


FIGURE 21 DRINKING WATER – DCPMU – BLANK VALUE, NO PEAK FOUND

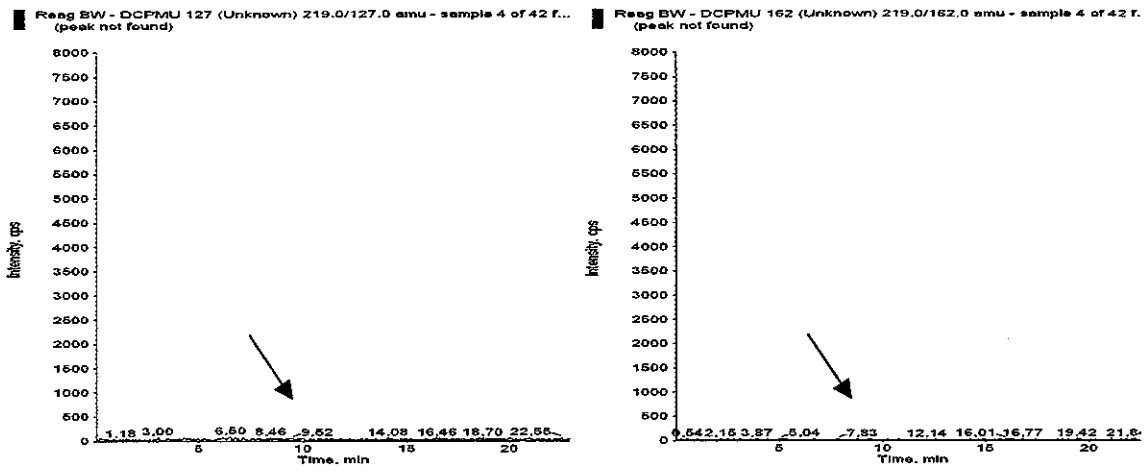


FIGURE 22 DRINKING WATER – DCPU – BLANK VALUE, NO PEAK FOUND

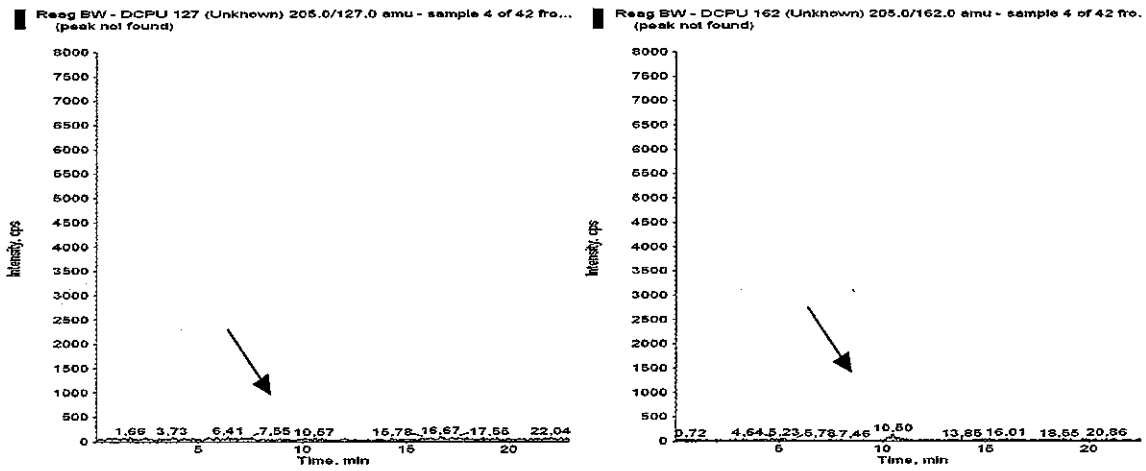


FIGURE 23 DRINKING WATER – DES. LINURON – BLANK VALUE, NO PEAK FOUND

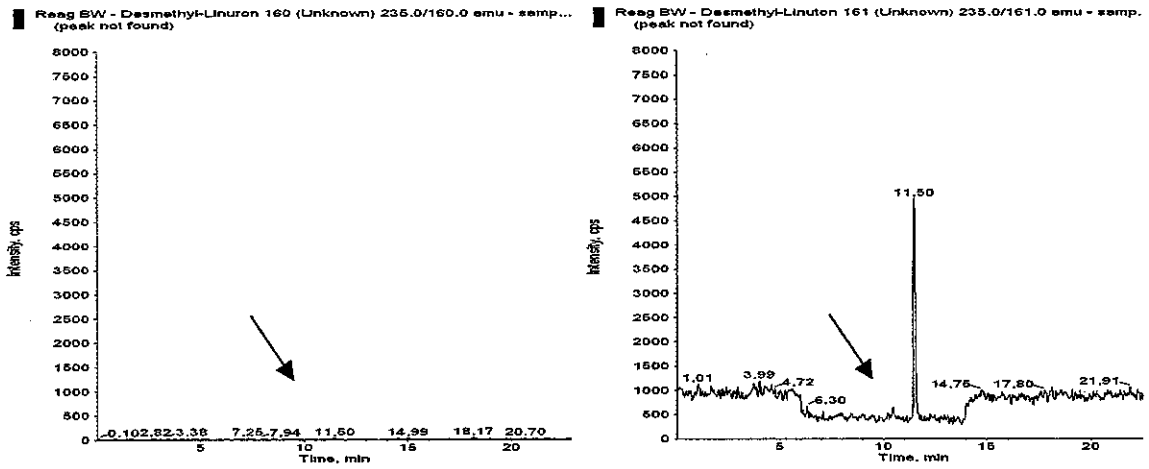


FIGURE 24 DRINKING WATER – MCPDMU – BLANK VALUE, NO PEAK FOUND

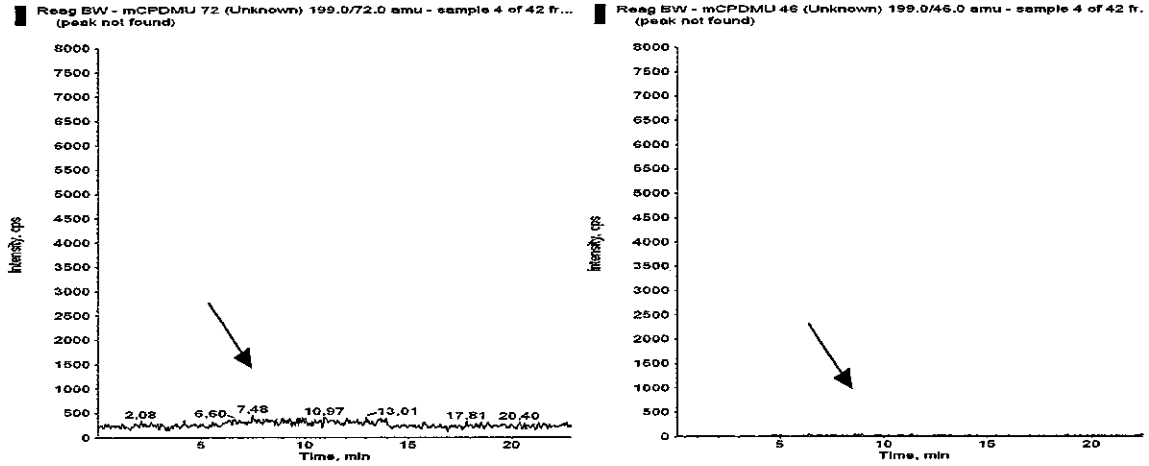


FIGURE 25 DRINKING WATER – DIURON – CONTROL SPECIMEN, NO PEAK FOUND

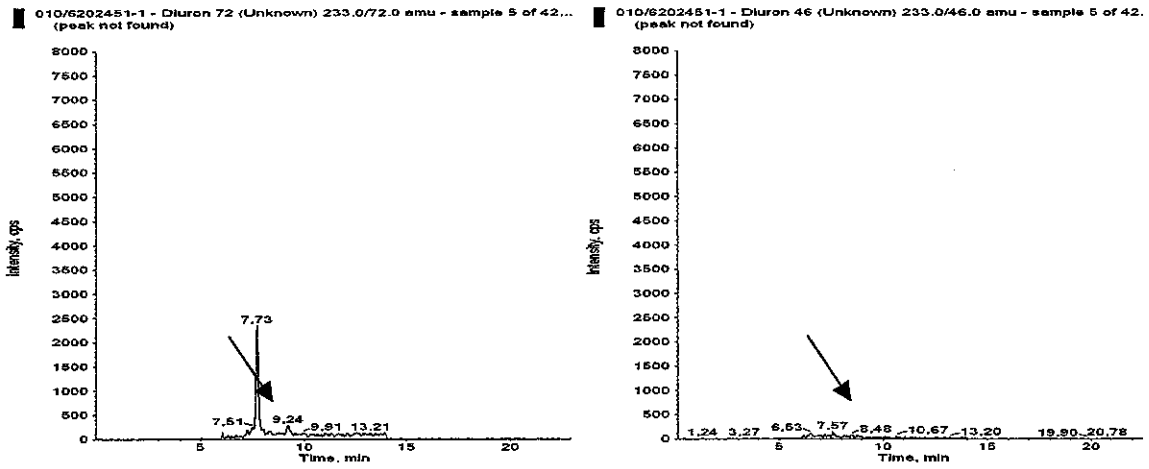


FIGURE 26 DRINKING WATER – LINURON – CONTROL SPECIMEN, NO PEAK FOUND

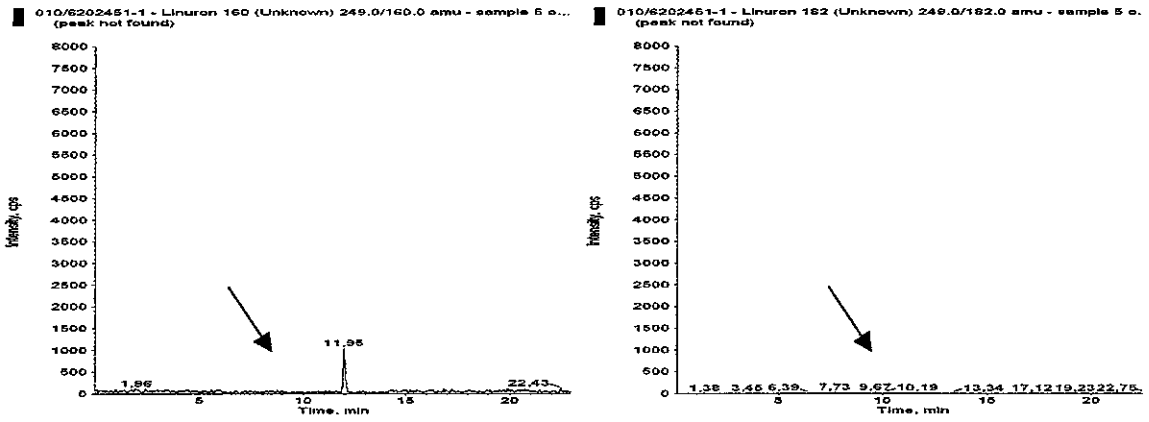


FIGURE 27 DRINKING WATER – DCPMU – CONTROL SPECIMEN, NO PEAK FOUND

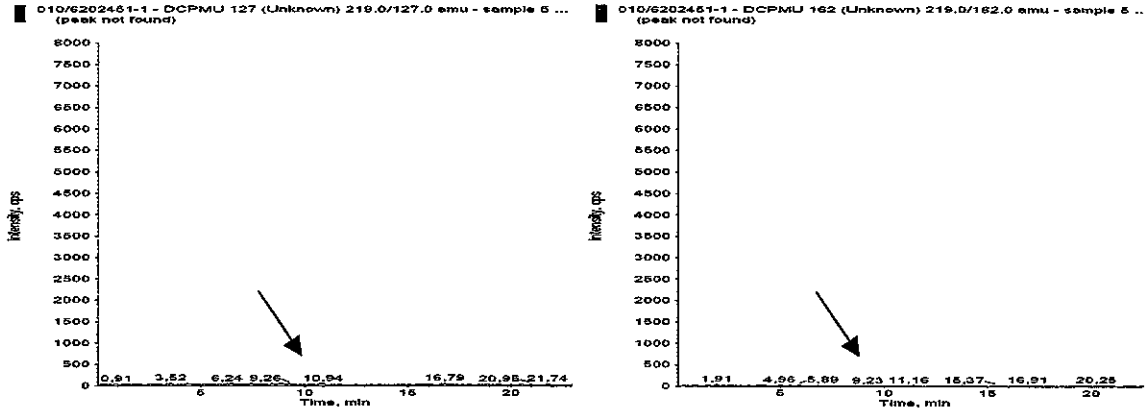


FIGURE 28 DRINKING WATER – DCPU – CONTROL SPECIMEN, NO PEAK FOUND

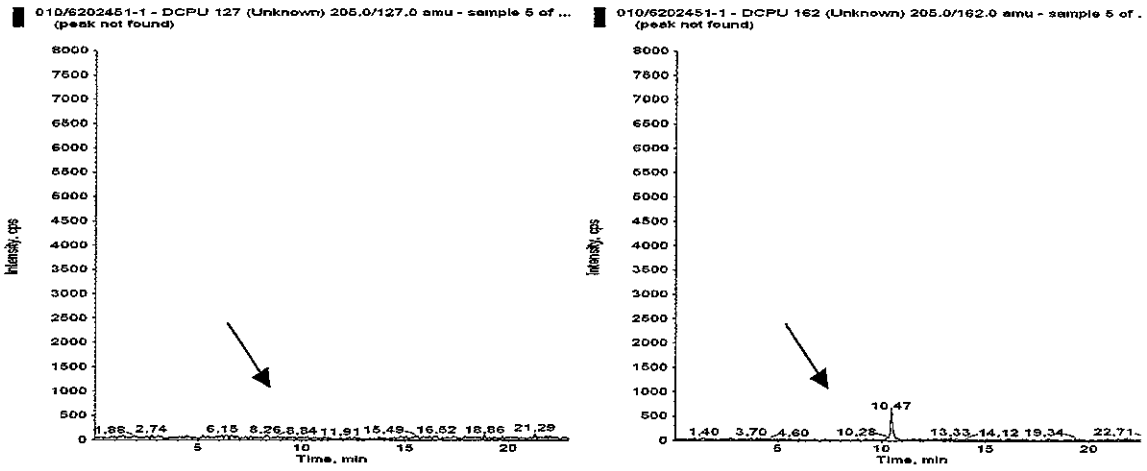


FIGURE 29 DRINKING WATER – DES. LINURON – CONTROL SPECIMEN, NO PEAK FOUND

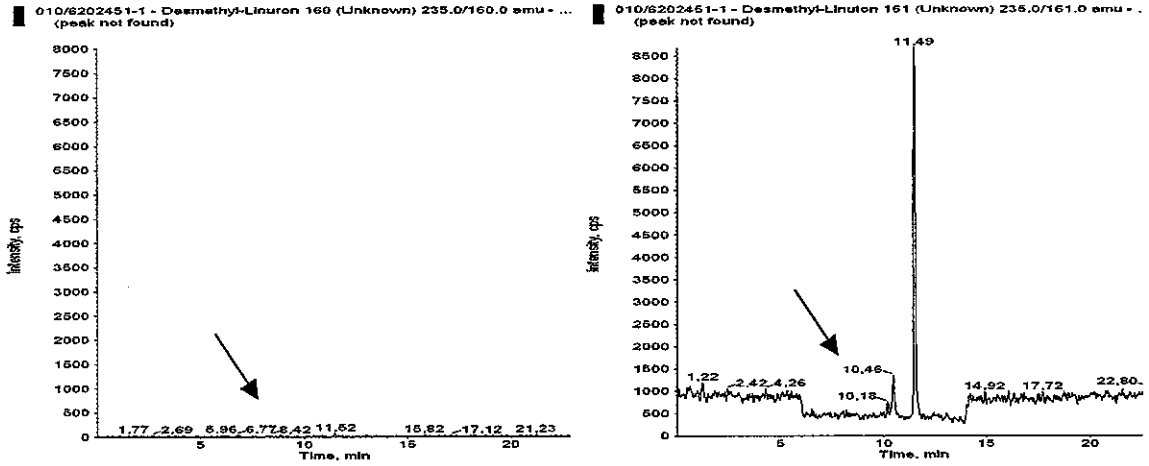


FIGURE 30 DRINKING WATER – MCPDMU – CONTROL SPECIMEN, NO PEAK FOUND

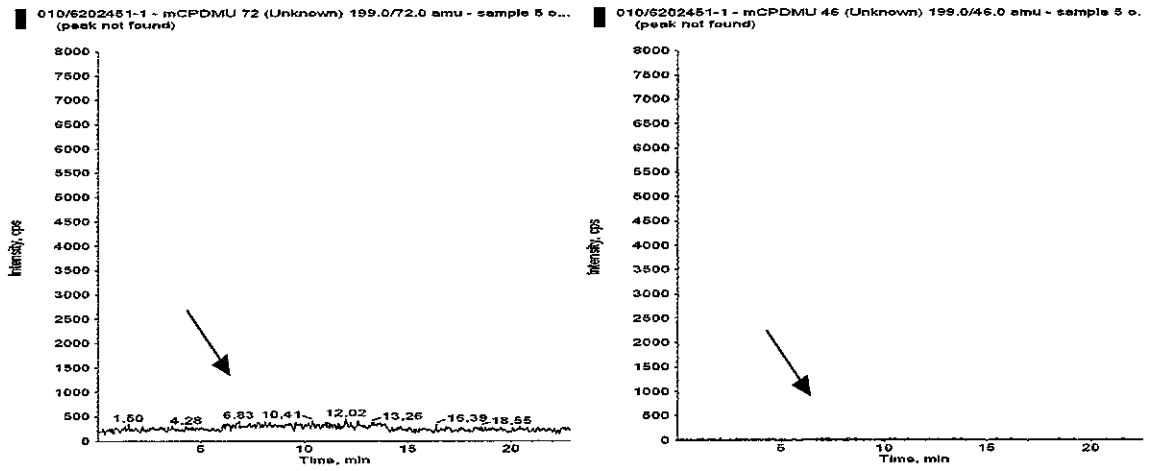


FIGURE 31 DRINKING WATER – DIURON – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 mL

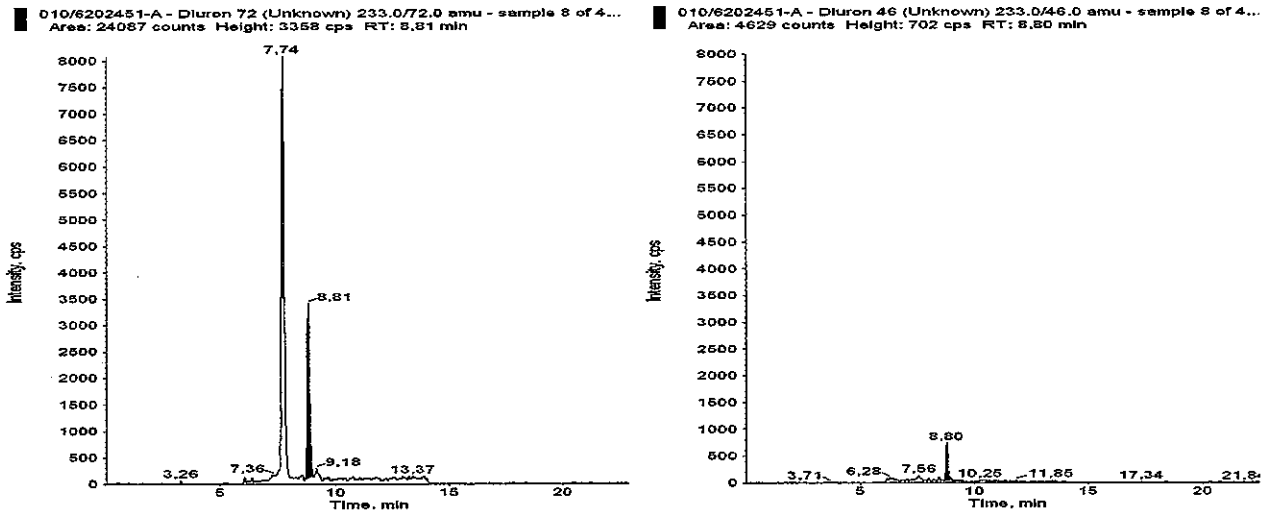


FIGURE 32 DRINKING WATER – LINURON – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 mL

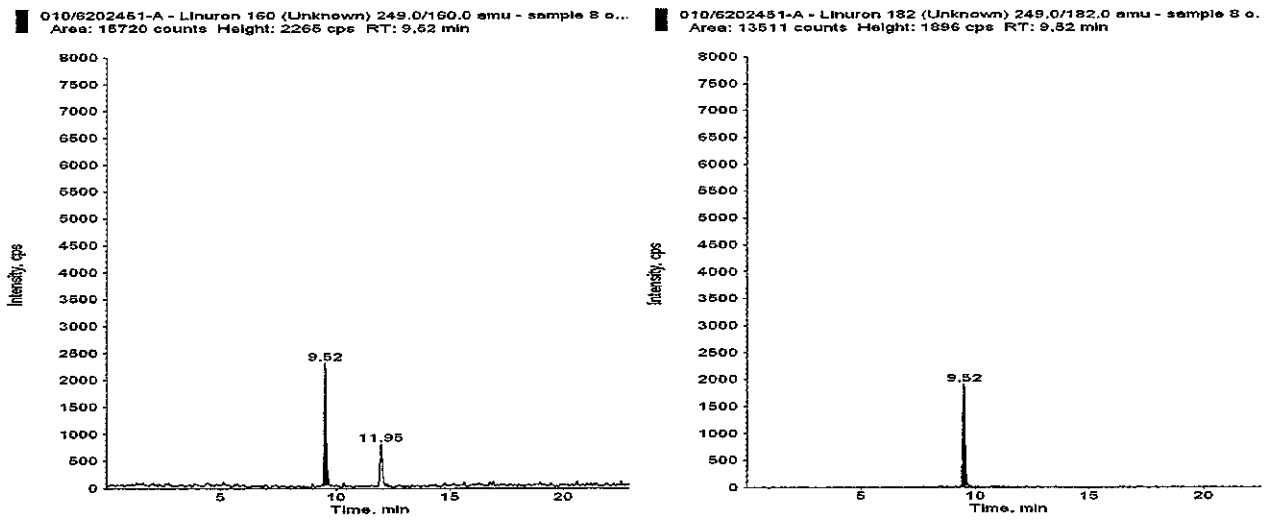


FIGURE 33 DRINKING WATER – DCPMU – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 ML

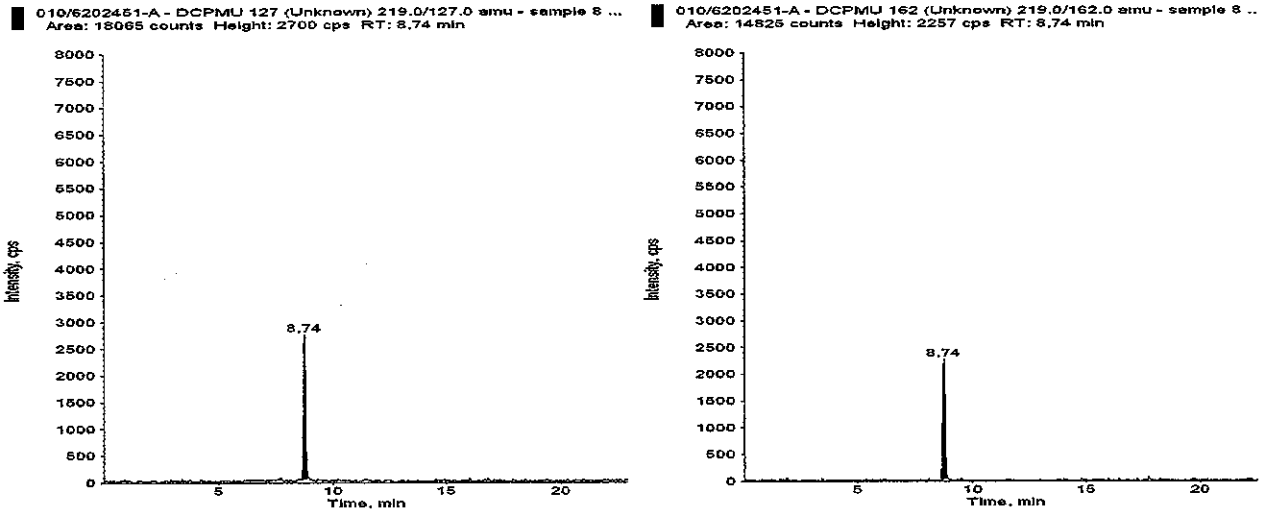


FIGURE 34 DRINKING WATER – DCPU – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 ML

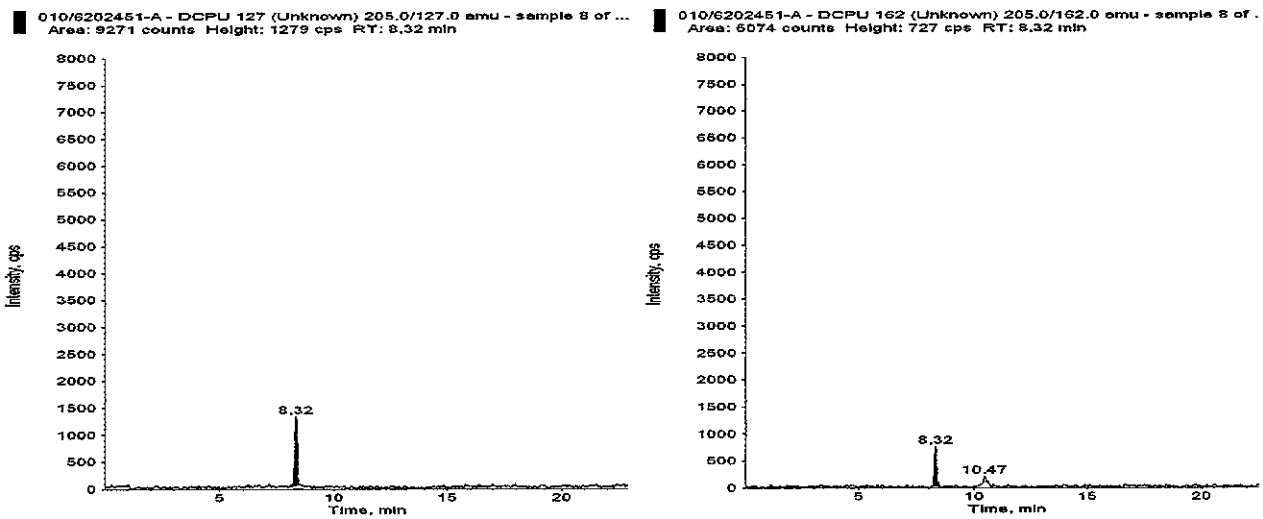


FIGURE 35 DRINKING WATER – DES. LINURON – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 ML

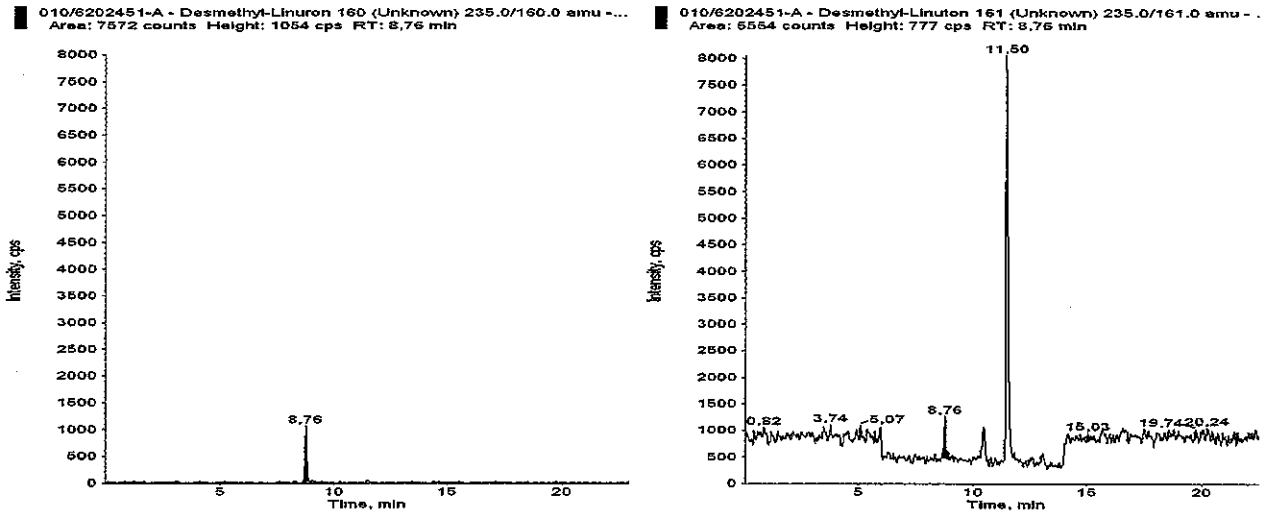


FIGURE 36 DRINKING WATER – MCPDMU – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 ML

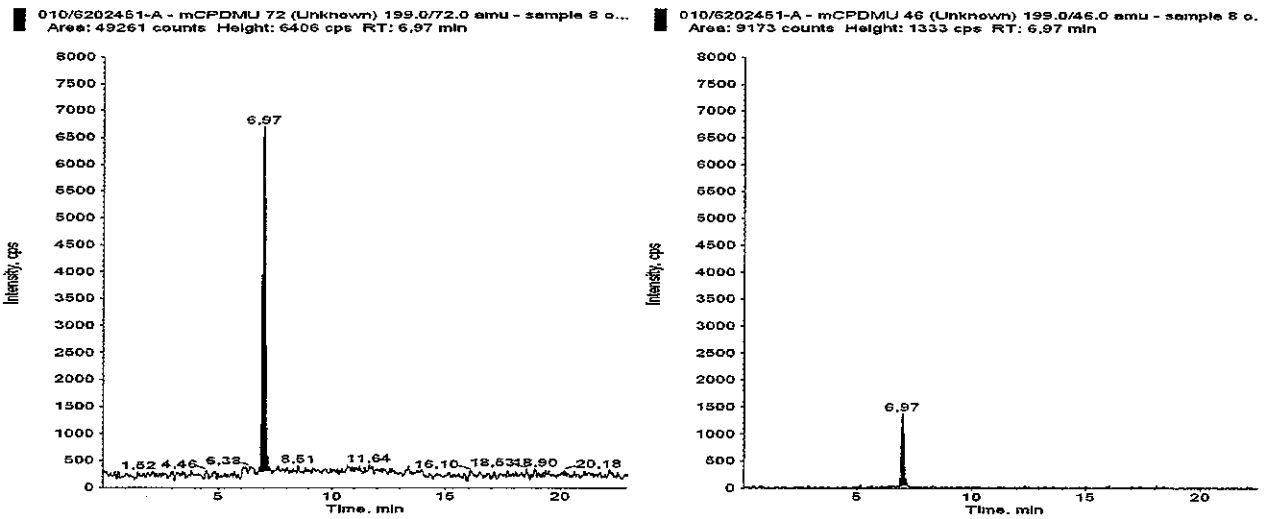


FIGURE 37 DRINKING WATER – DIURON – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 ML

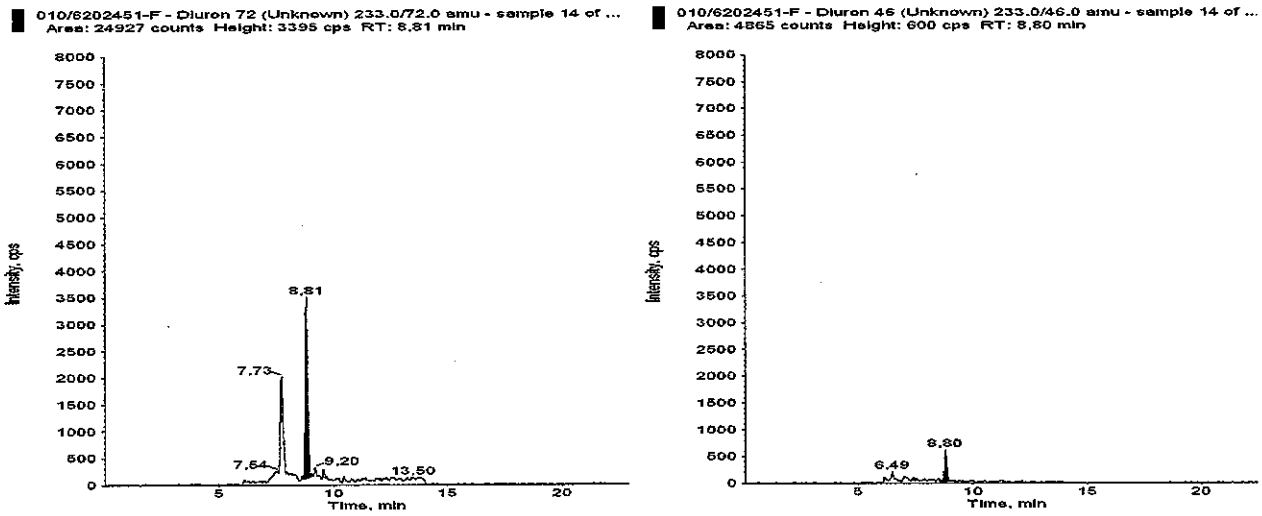


FIGURE 38 DRINKING WATER – LINURON – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 ML

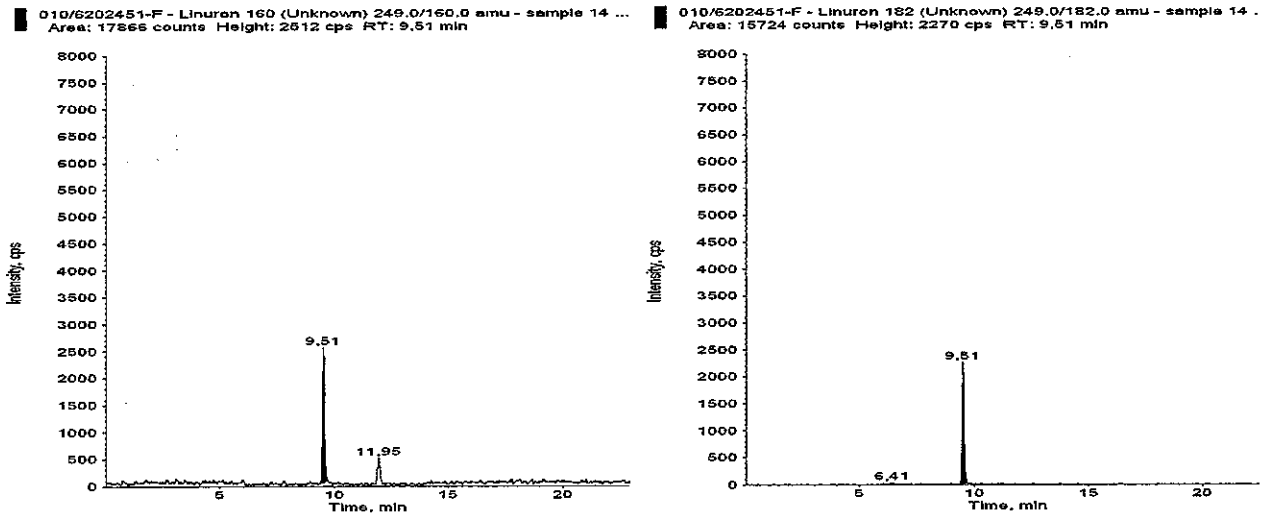


FIGURE 39 DRINKING WATER – DCPMU – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 ML

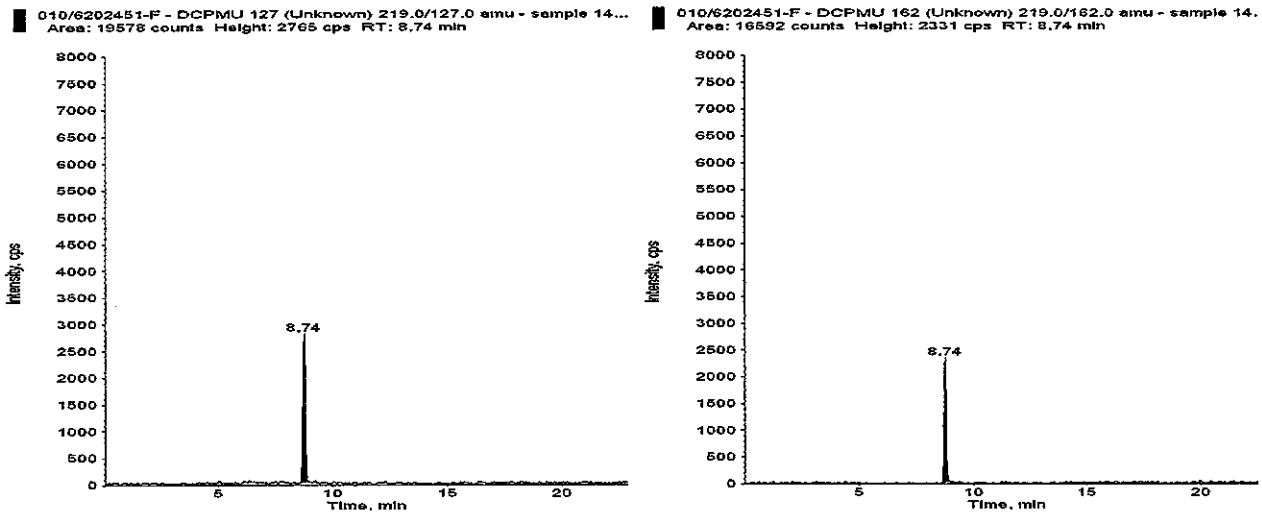


FIGURE 40 DRINKING WATER – DCPU – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 ML

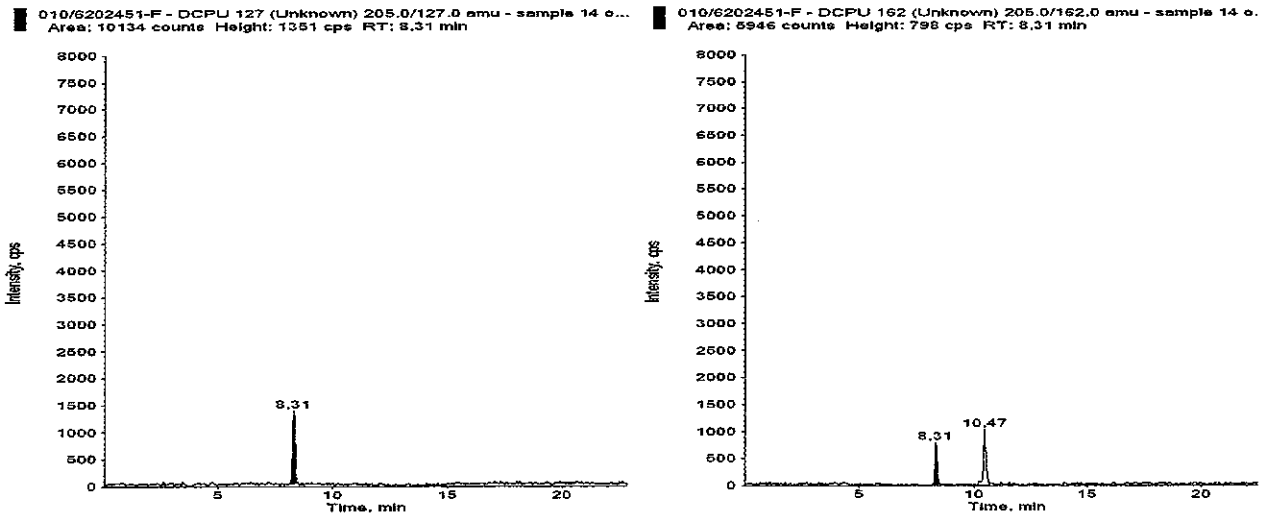


FIGURE 41 DRINKING WATER – DES. LINURON – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 ML

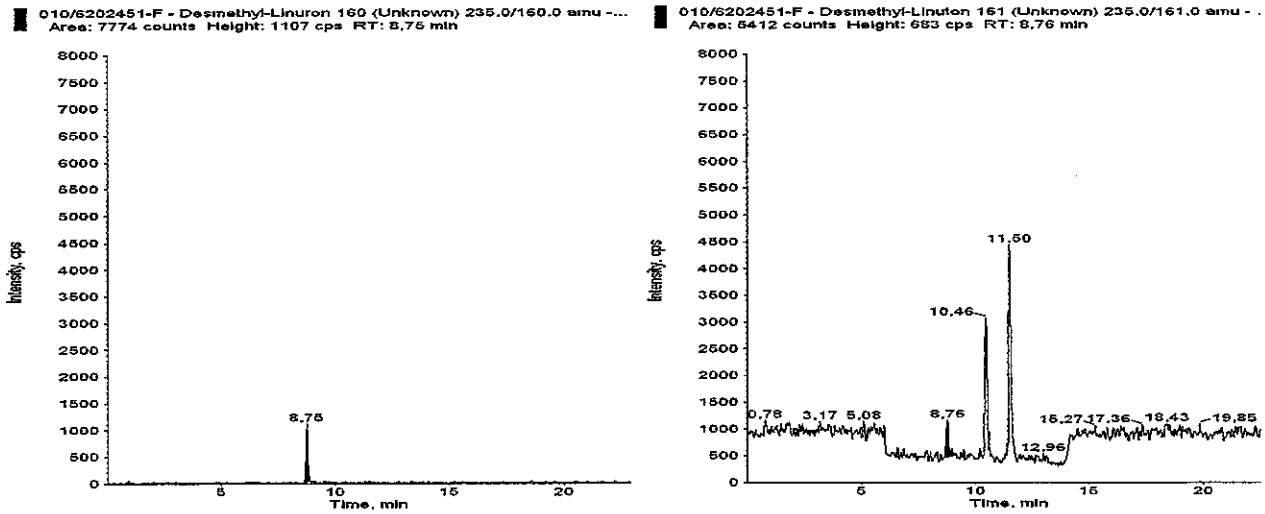


FIGURE 42 DRINKING WATER – MCPDMU – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 ML

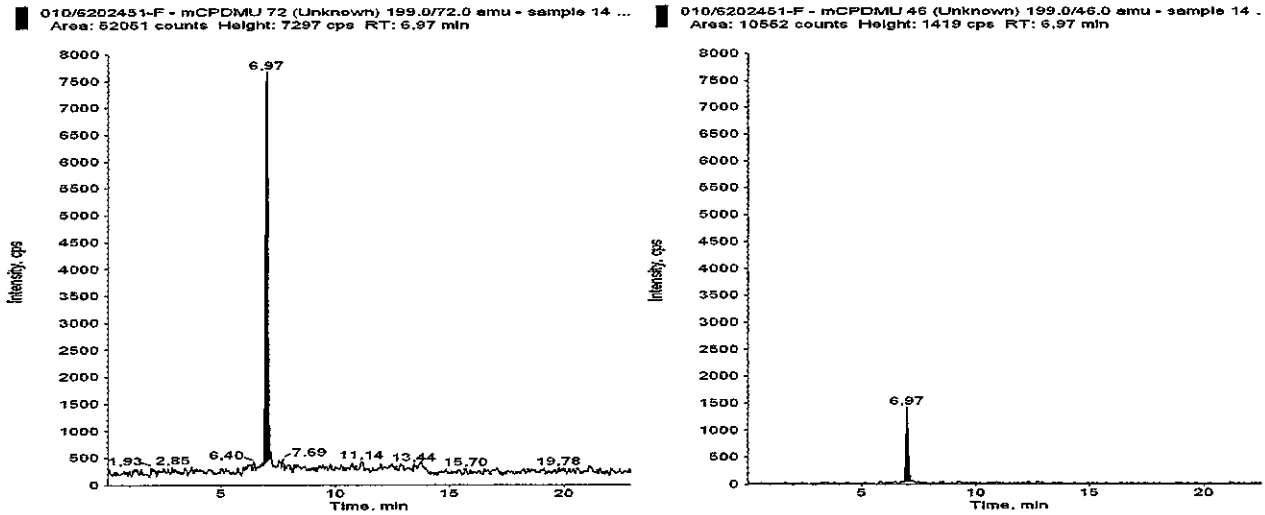


FIGURE 43 SURFACE WATER – DIURON – STANDARD SOLUTION 1 NG/ML

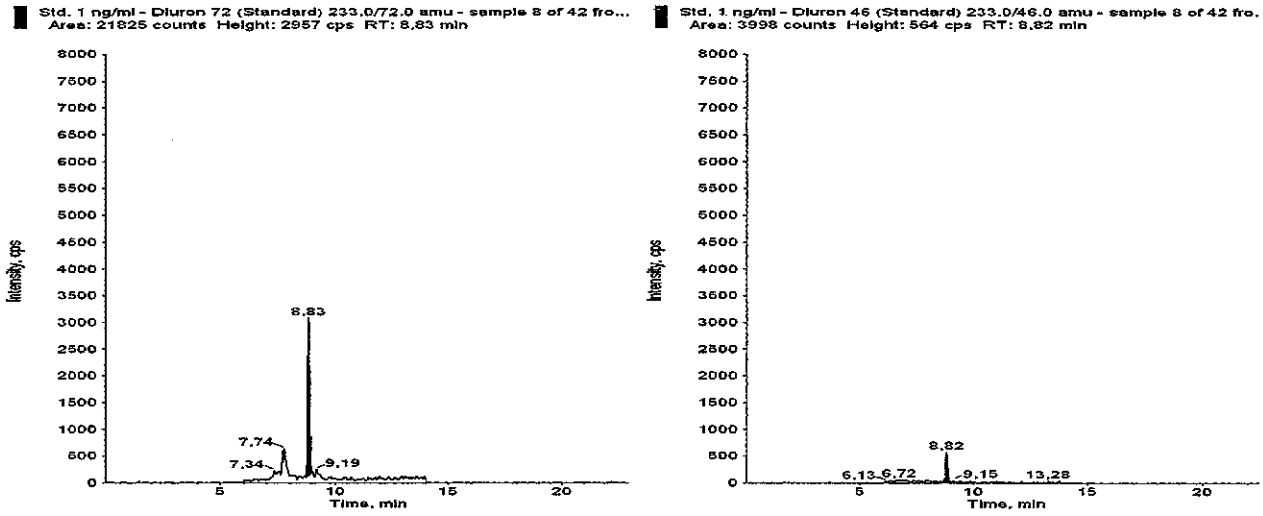


FIGURE 44 SURFACE WATER – LINURON – STANDARD SOLUTION 1 NG/ML

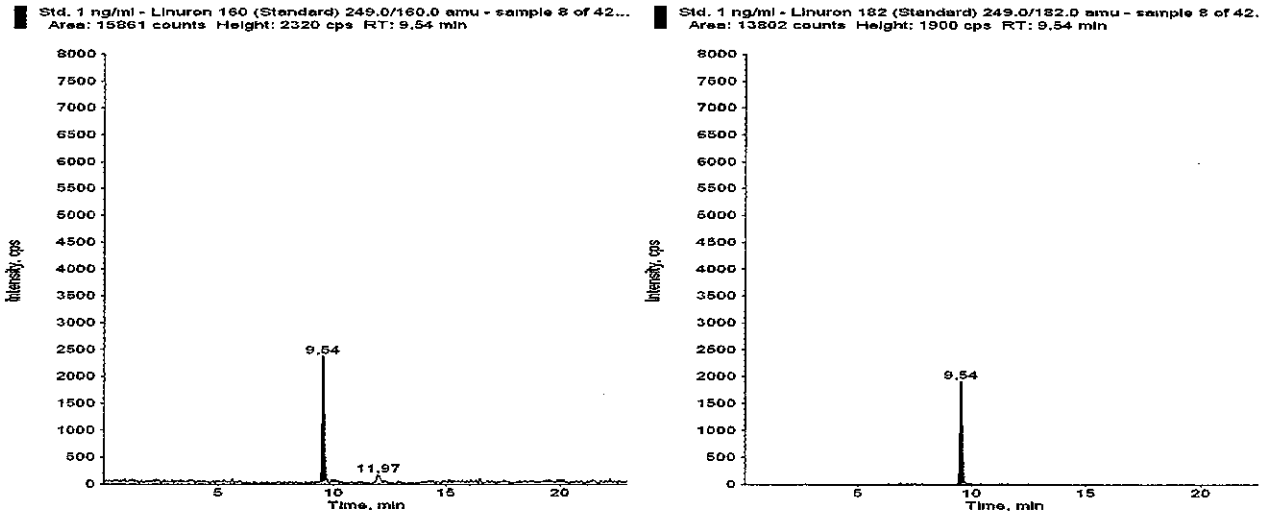


FIGURE 45 SURFACE WATER – DCPMU – STANDARD SOLUTION 1 NG/ML

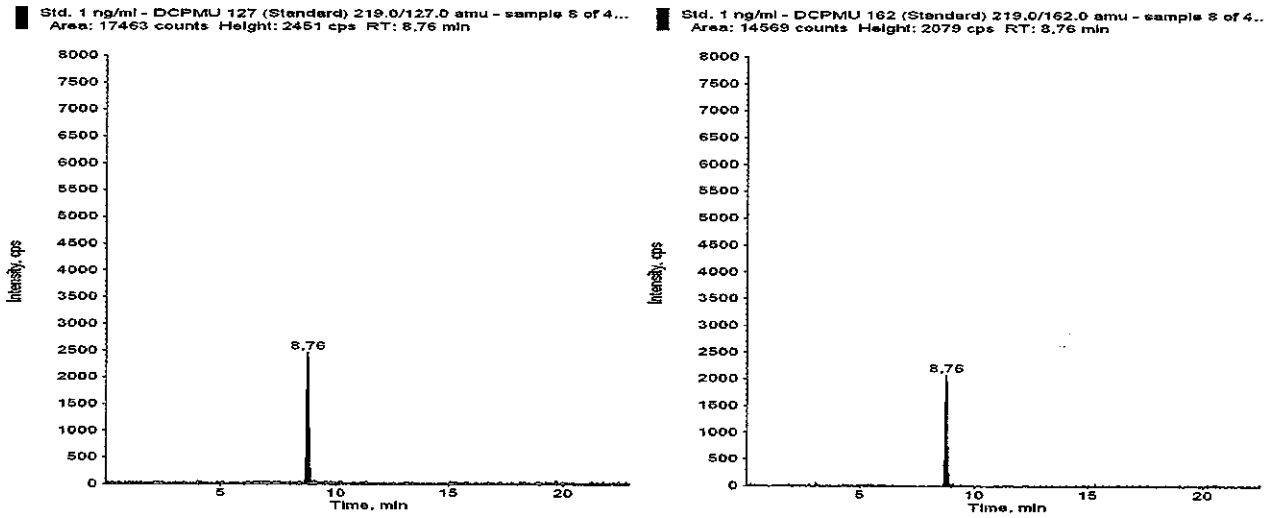


FIGURE 46 SURFACE WATER – DCPU – STANDARD SOLUTION 1 NG/ML

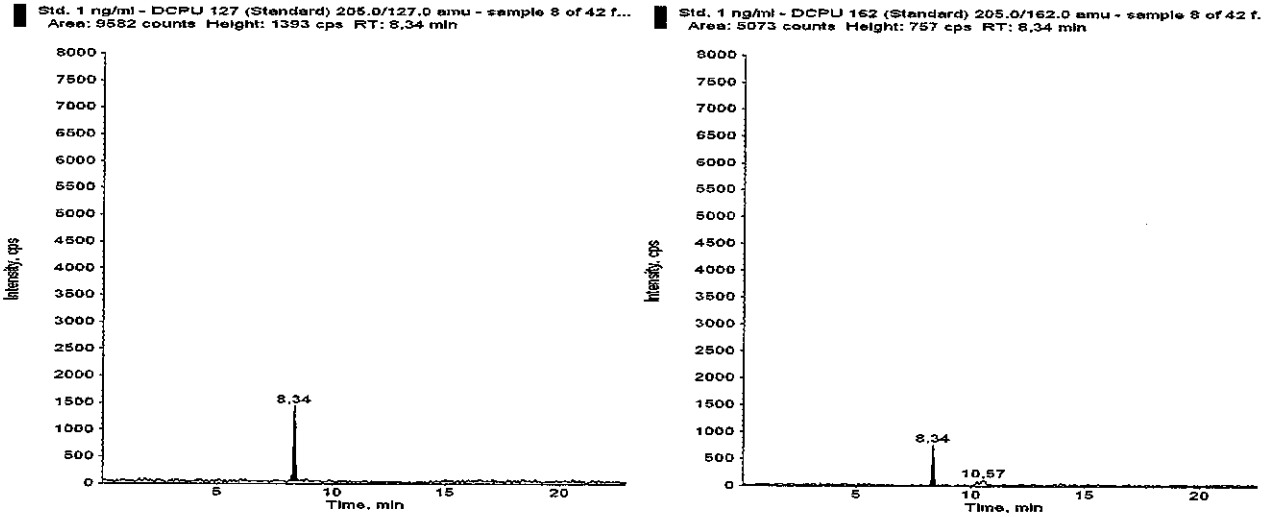


FIGURE 47 SURFACE WATER – DES. LINURON – STANDARD SOLUTION 1 NG/ML

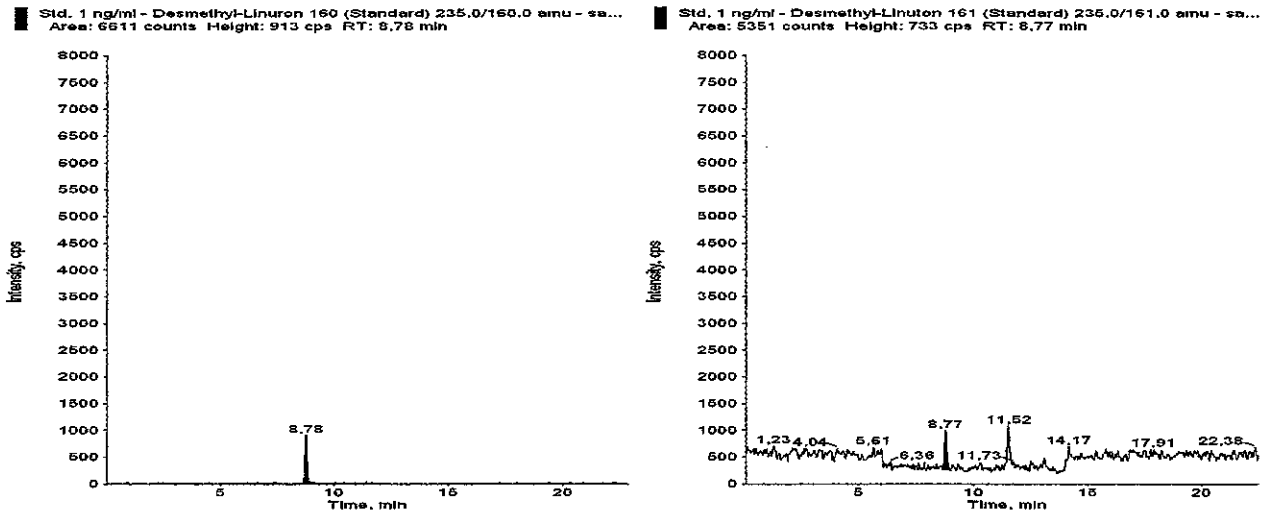


FIGURE 48 SURFACE WATER – MCPDMU – STANDARD SOLUTION 1 NG/ML

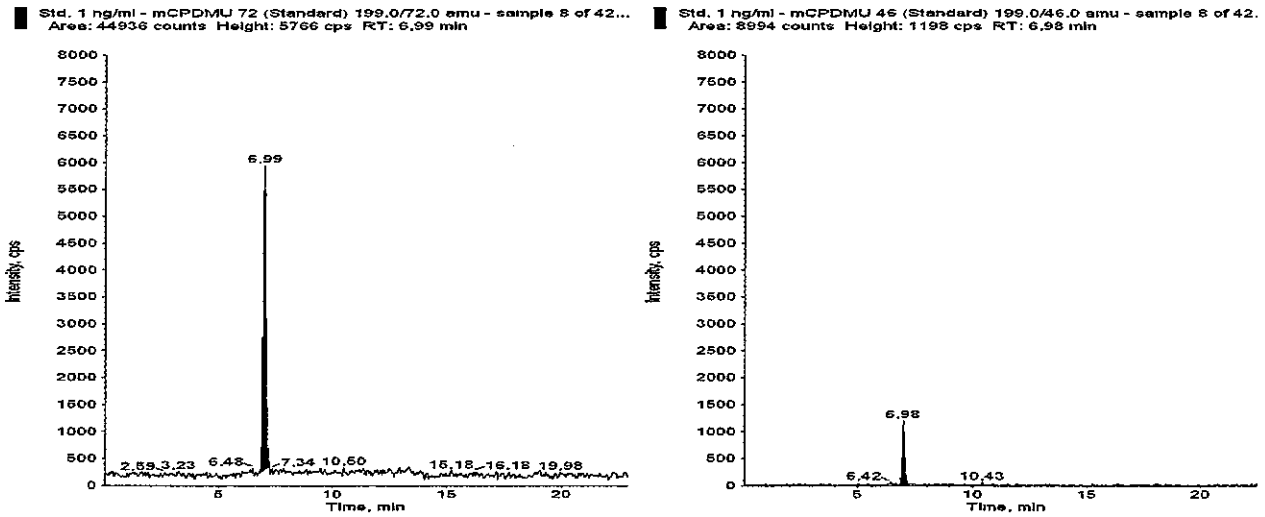


FIGURE 49 SURFACE WATER – DIURON – BLANK VALUE, NO PEAK FOUND

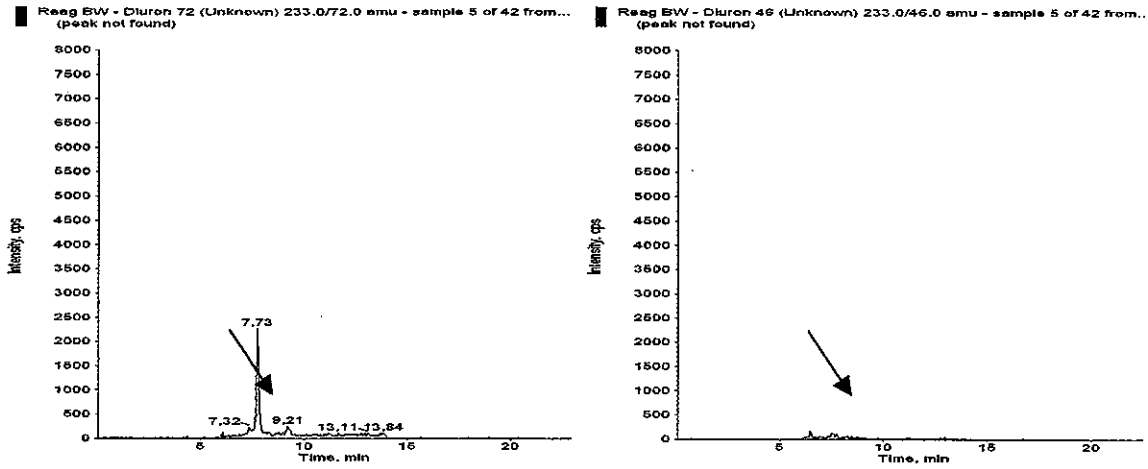


FIGURE 50 SURFACE WATER – LINURON – BLANK VALUE, NO PEAK FOUND

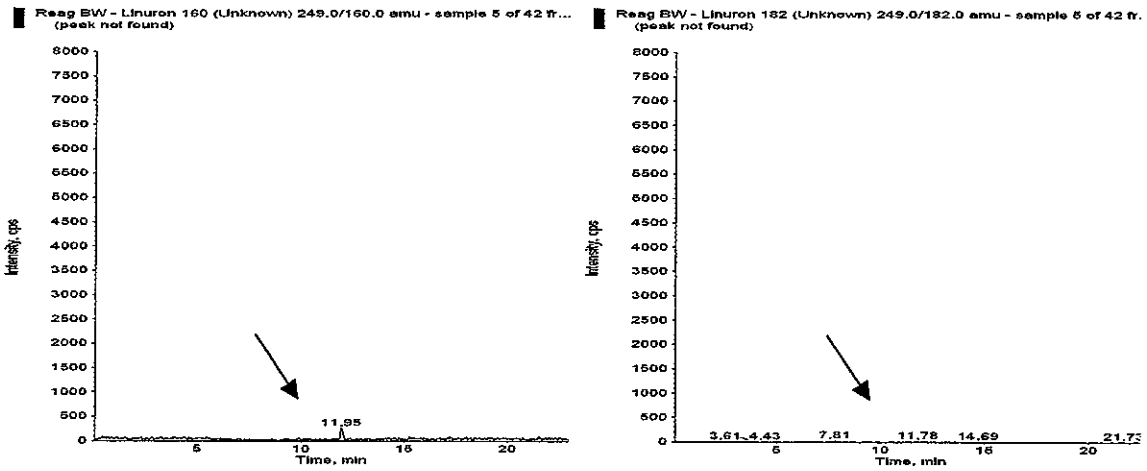


FIGURE 51 SURFACE WATER – DCPMU – BLANK VALUE, NO PEAK FOUND

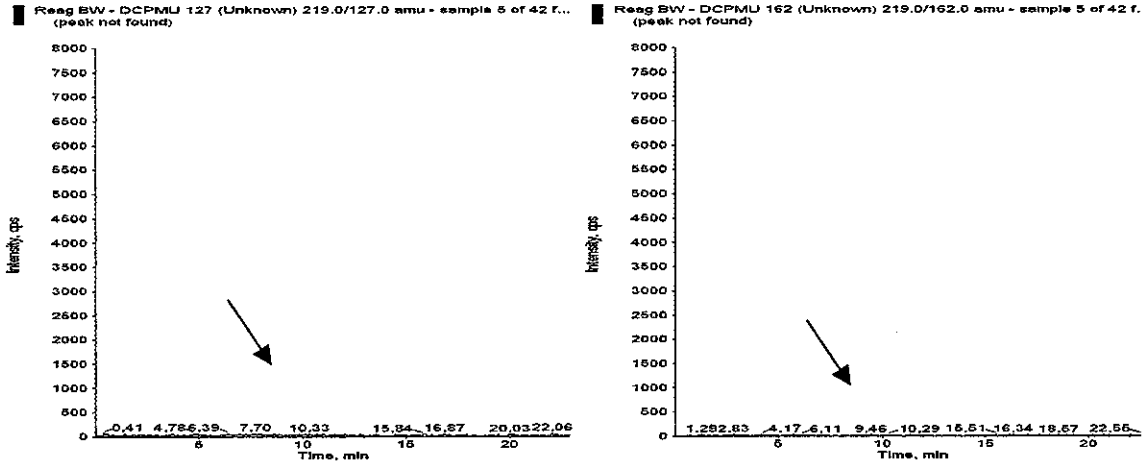


FIGURE 52 SURFACE WATER – DCPU – BLANK VALUE, NO PEAK FOUND

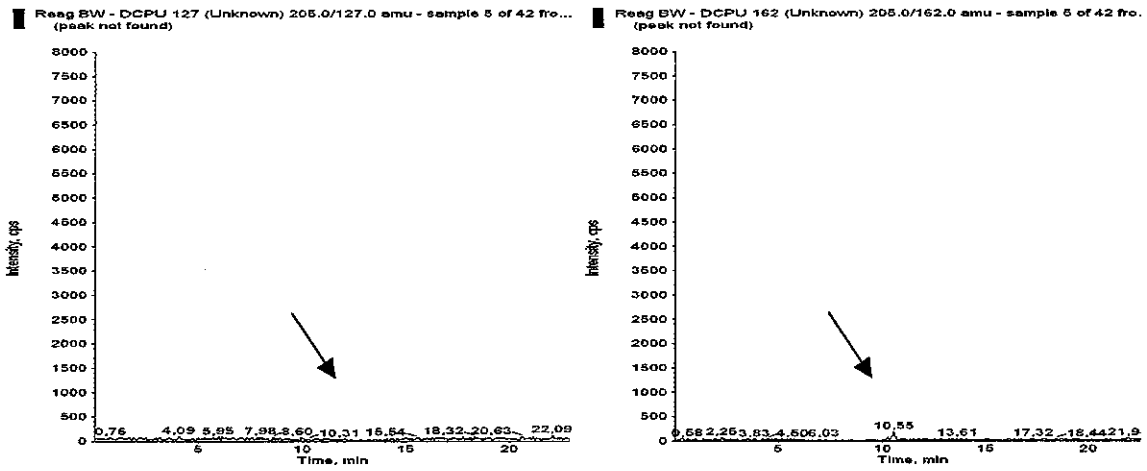


FIGURE 53 SURFACE WATER – DES. LINURON – BLANK VALUE, NO PEAK FOUND

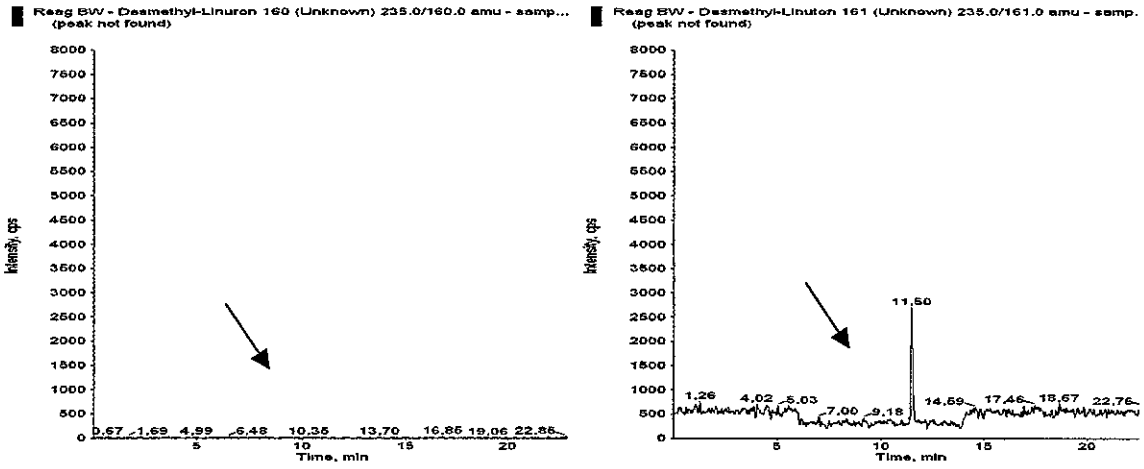


FIGURE 54 SURFACE WATER – MCPDMU – BLANK VALUE, NO PEAK FOUND

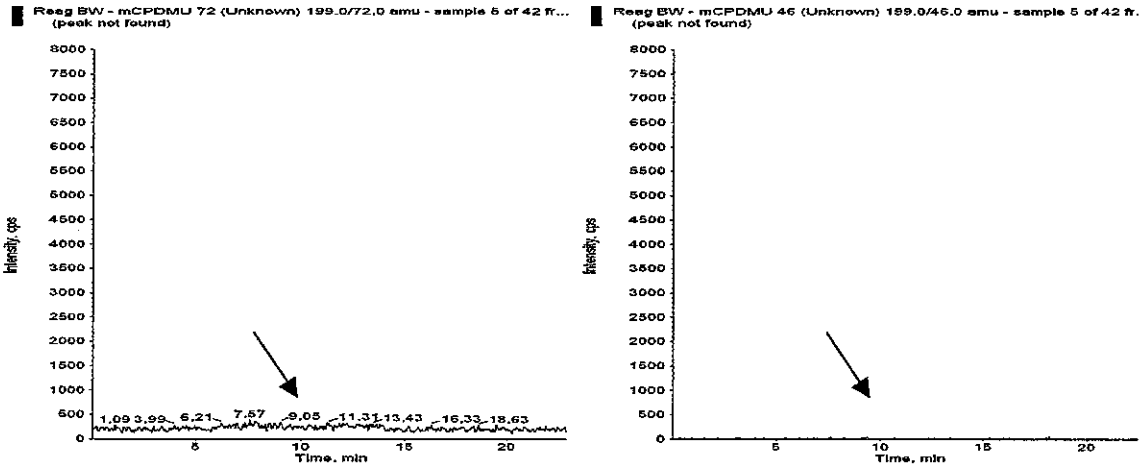


FIGURE 55 SURFACE WATER – DIURON – CONTROL SPECIMEN, SMALL PEAK WELL BELOW 30% LOQ WAS FOUND, FINAL VOLUME 1 mL

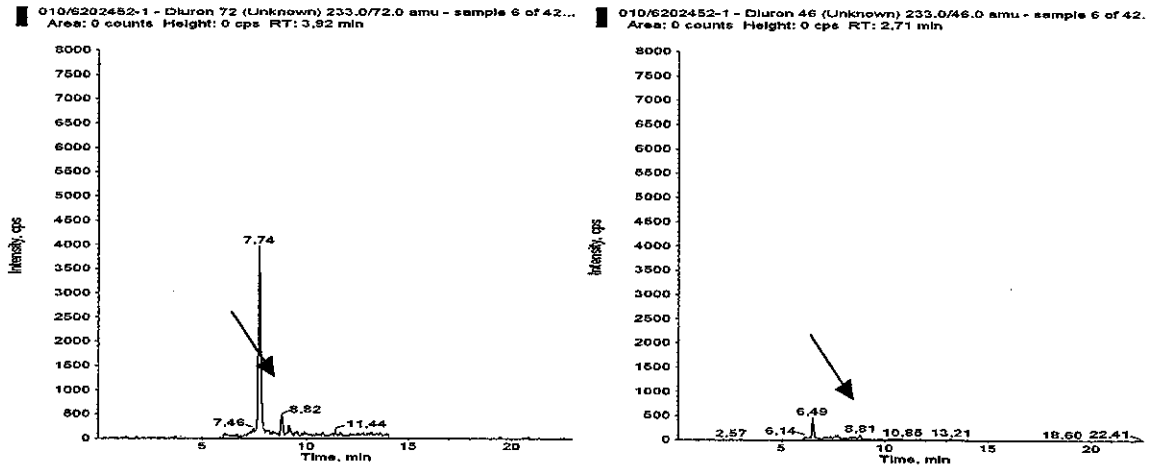


FIGURE 56 SURFACE WATER – LINURON – CONTROL SPECIMEN, NO PEAK FOUND, FINAL VOLUME 1 mL

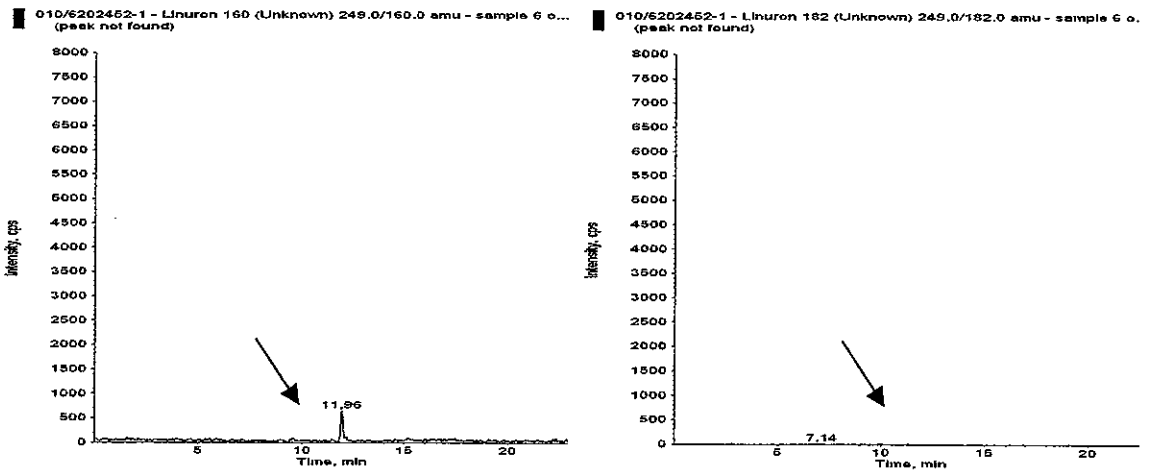


FIGURE 57 SURFACE WATER – DCPMU – CONTROL SPECIMEN, SMALL PEAK WELL BELOW 30% LOQ WAS FOUND, FINAL VOLUME 1 ML

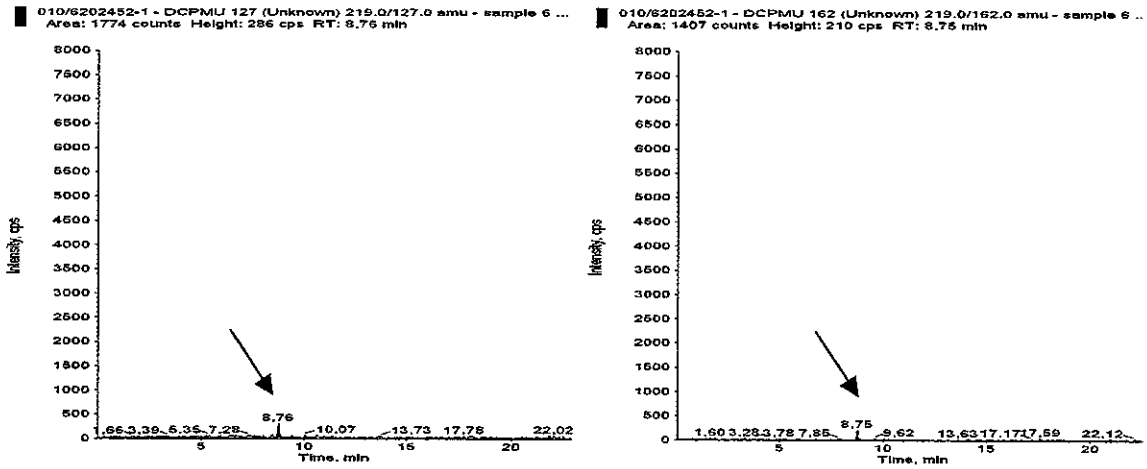


FIGURE 58 SURFACE WATER – DCPU – CONTROL SPECIMEN, NO PEAK FOUND, FINAL VOLUME 1 ML

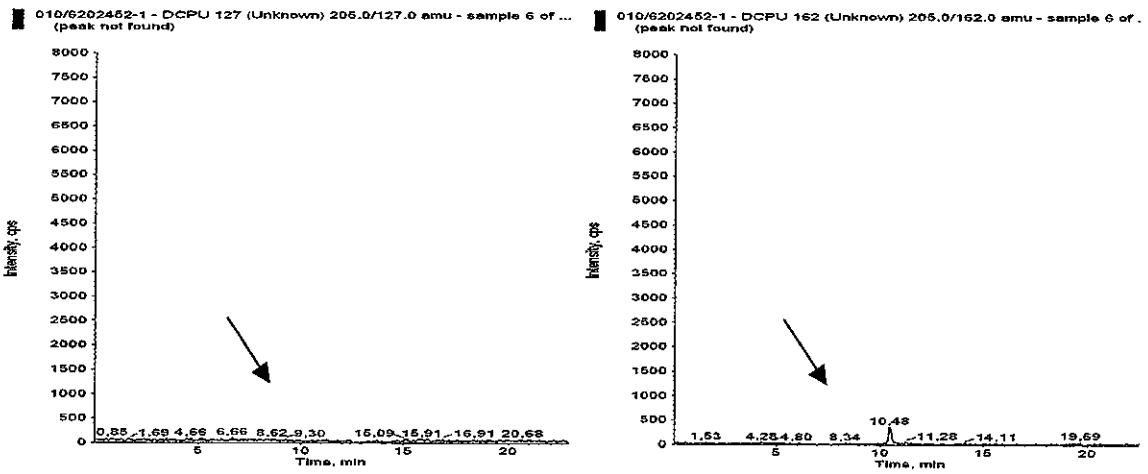


FIGURE 59 SURFACE WATER – DES. LINURON – CONTROL SPECIMEN, NO PEAK FOUND, FINAL VOLUME 1 mL

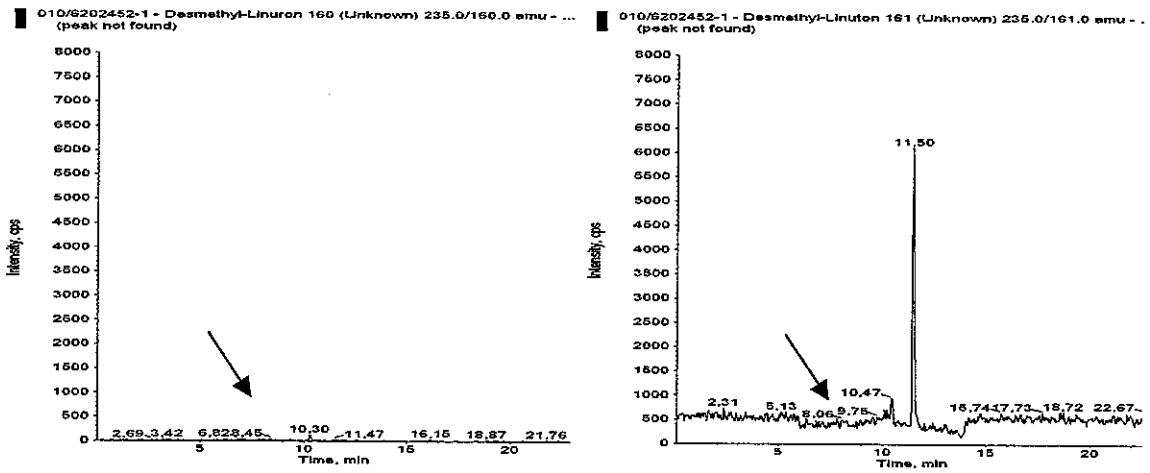


FIGURE 60 SURFACE WATER – MCPDMU – CONTROL SPECIMEN, NO PEAK FOUND, FINAL VOLUME 1 mL

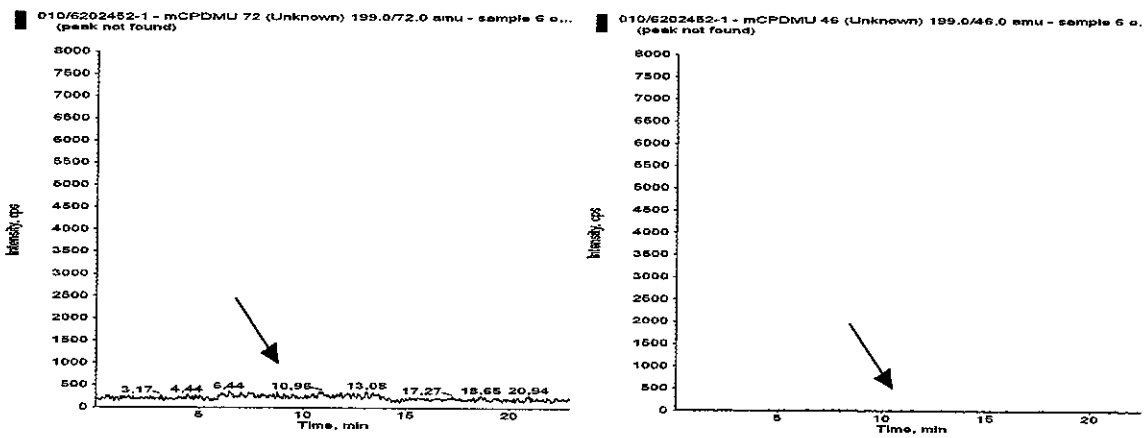


FIGURE 61 SURFACE WATER – DIURON – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 mL

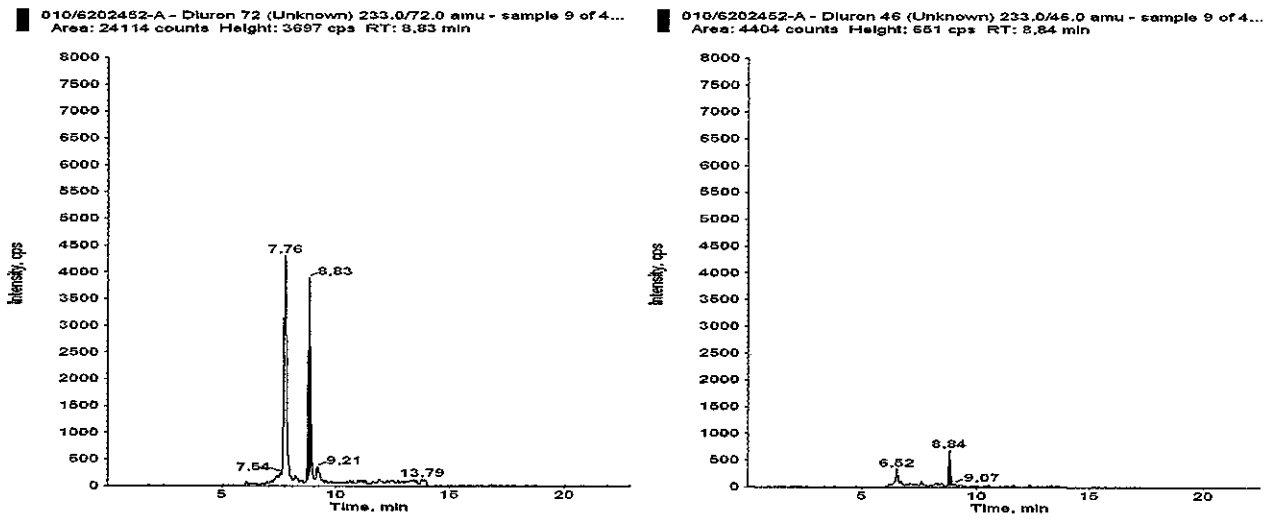


FIGURE 62 SURFACE WATER – LINURON – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 mL

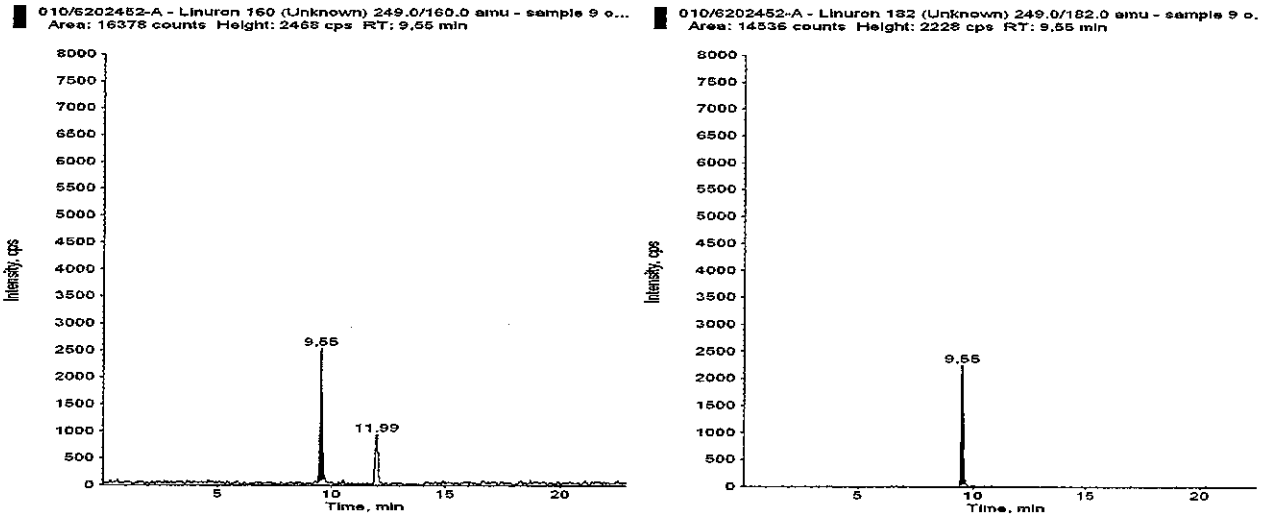


FIGURE 63 SURFACE WATER – DCPMU – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 mL

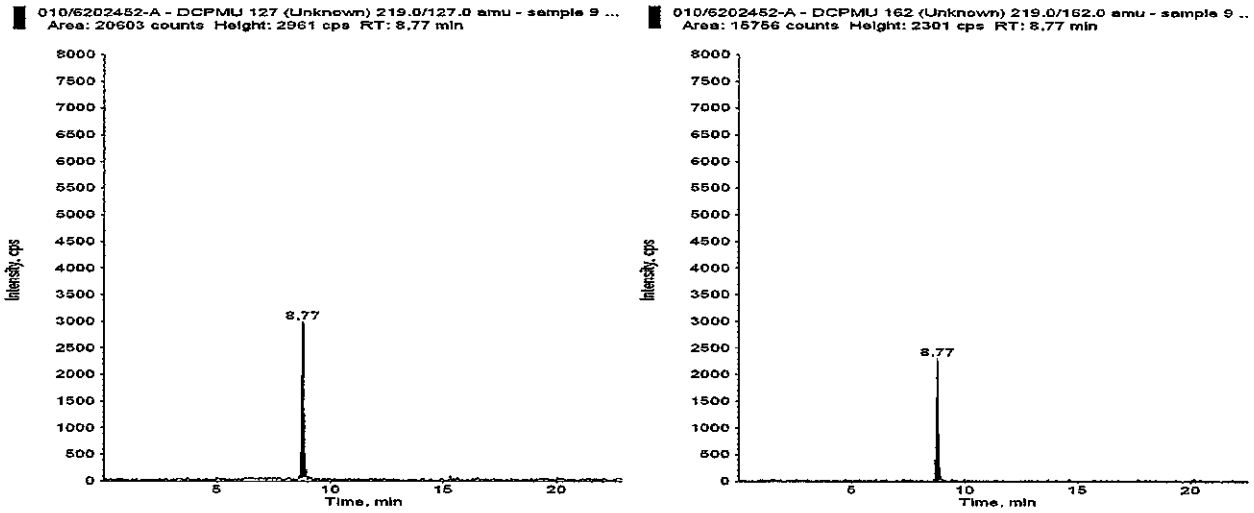


FIGURE 64 SURFACE WATER – DCPU – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 mL

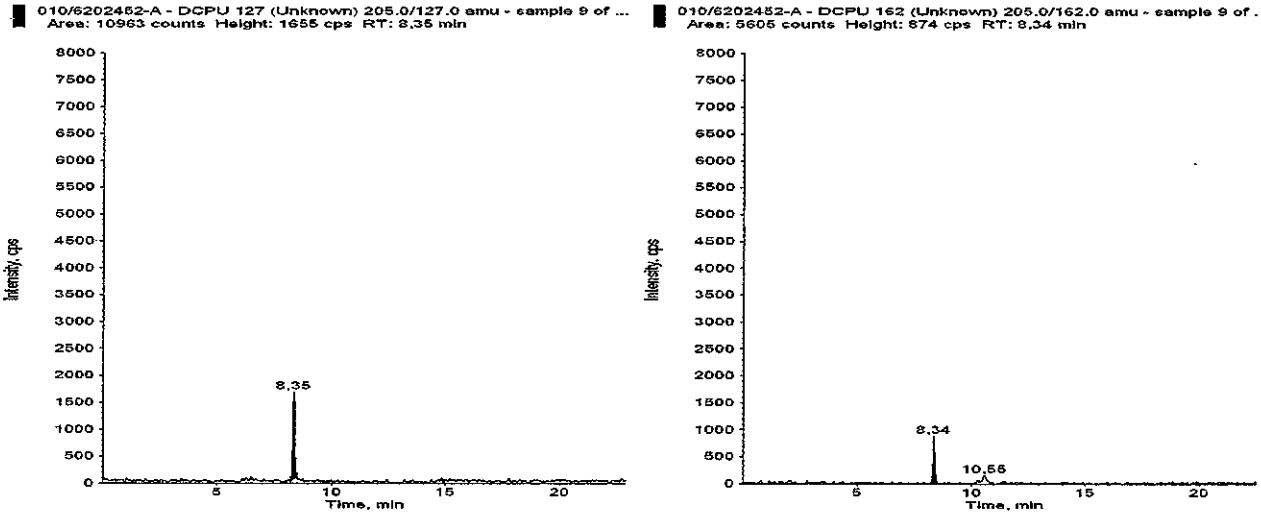


FIGURE 65 SURFACE WATER – DES. LINURON – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 ML

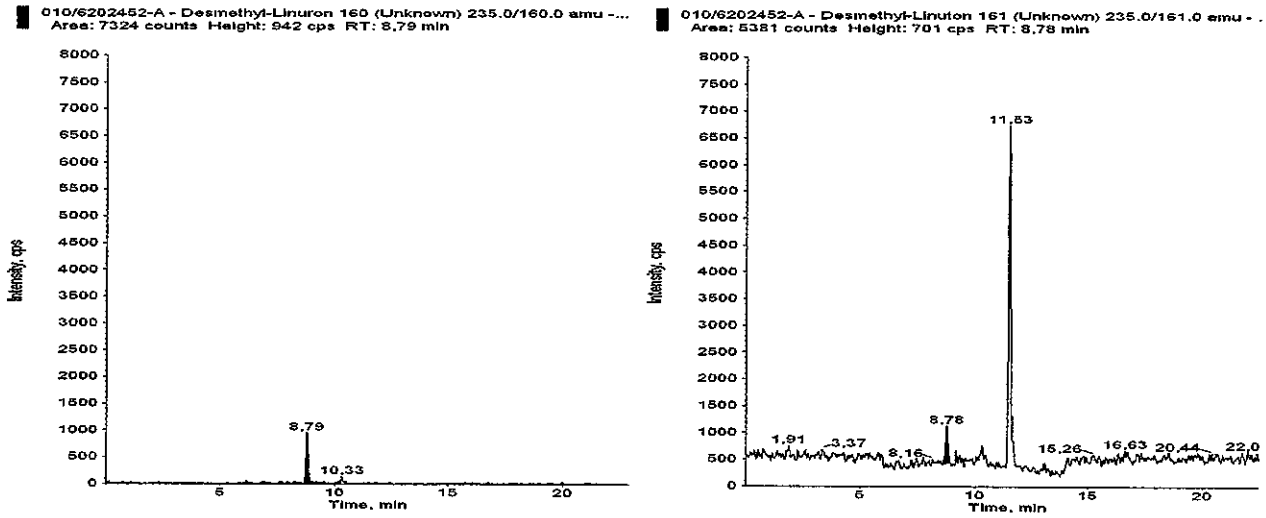


FIGURE 66 SURFACE WATER – MCPDMU – FORTIFIED SPECIMEN, LOQ, FINAL VOLUME 1 ML

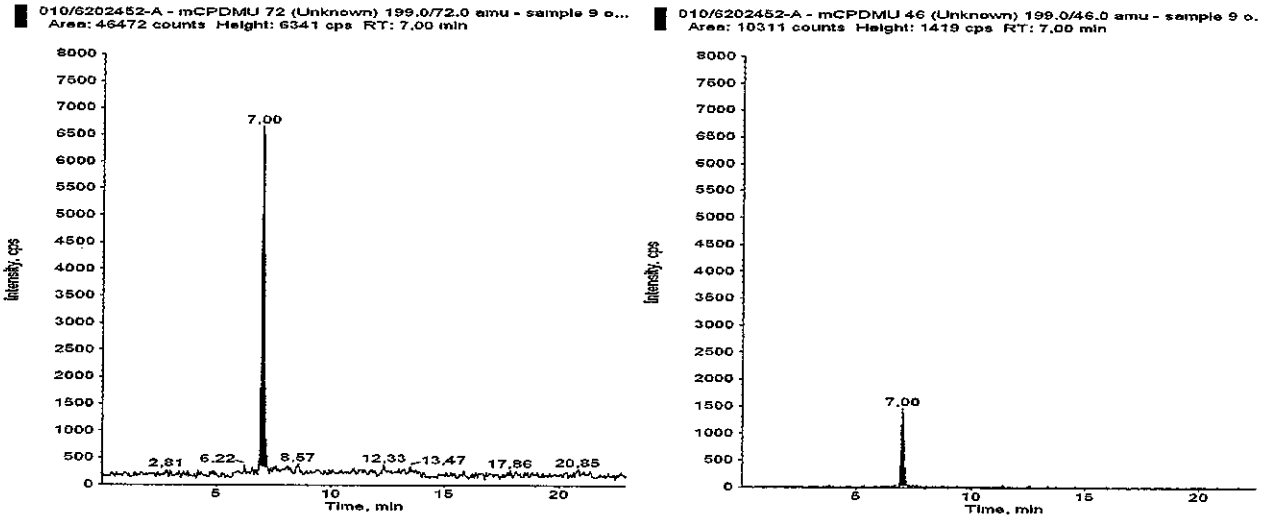


FIGURE 67 SURFACE WATER – DIURON – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 mL

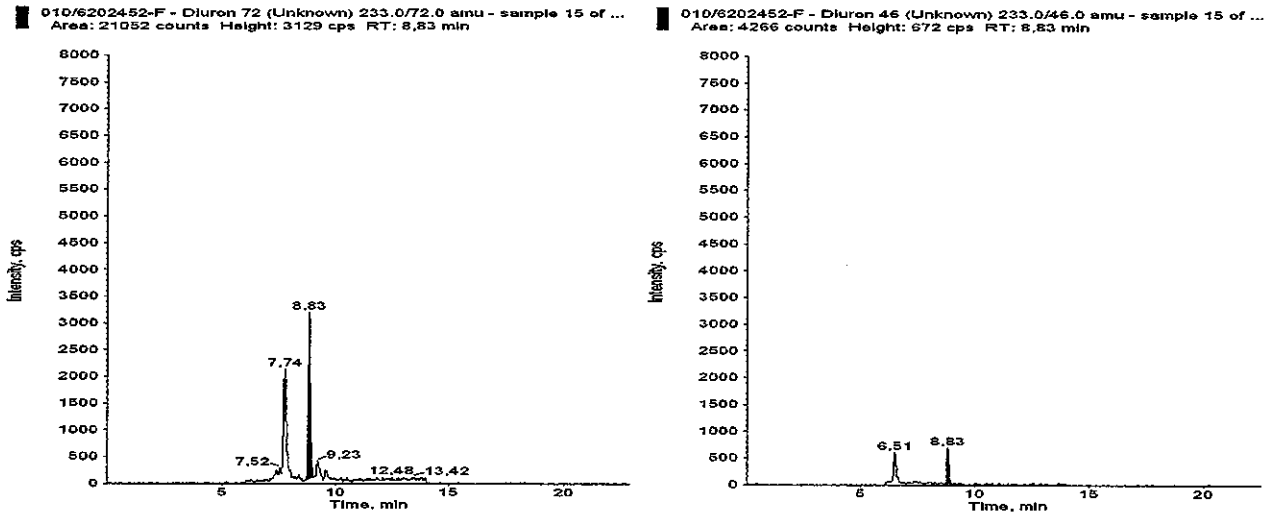


FIGURE 68 SURFACE WATER – LINURON – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 mL

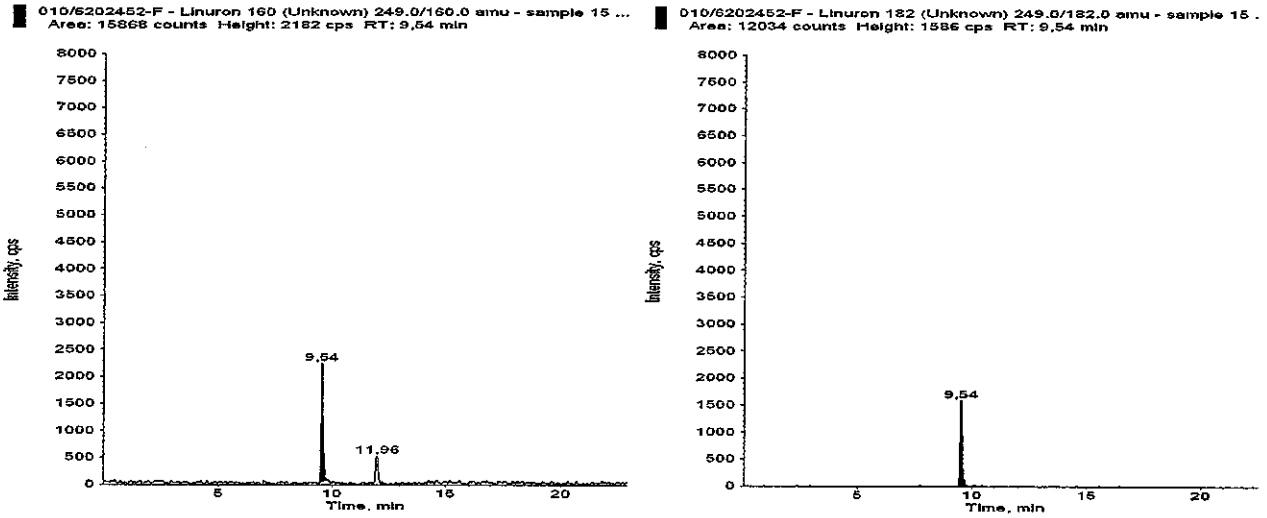


FIGURE 69 SURFACE WATER – DCPMU – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 ML

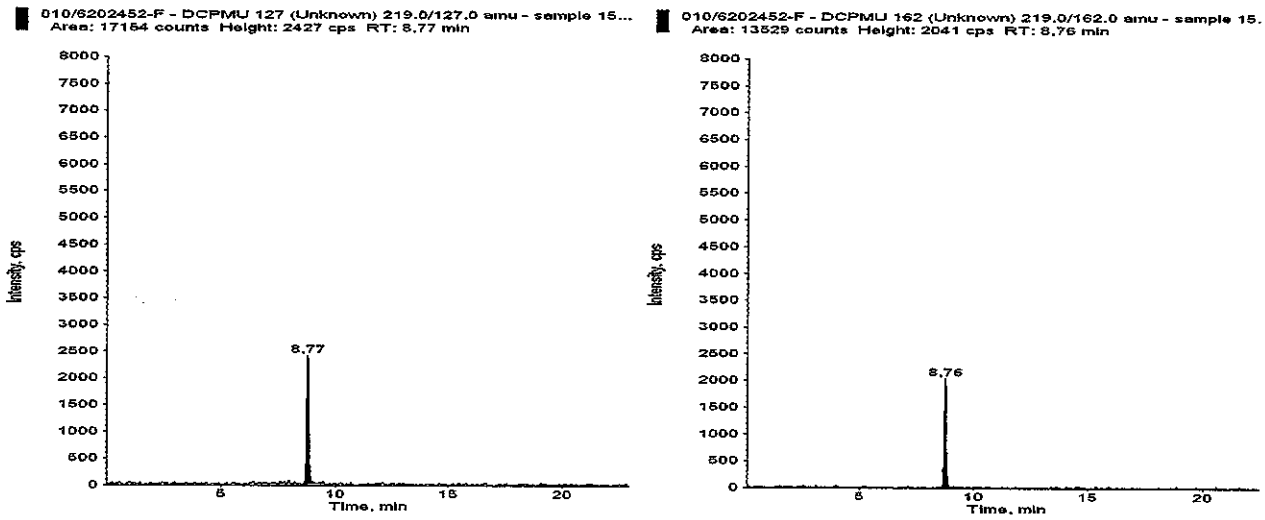


FIGURE 70 SURFACE WATER – DCPU – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 ML

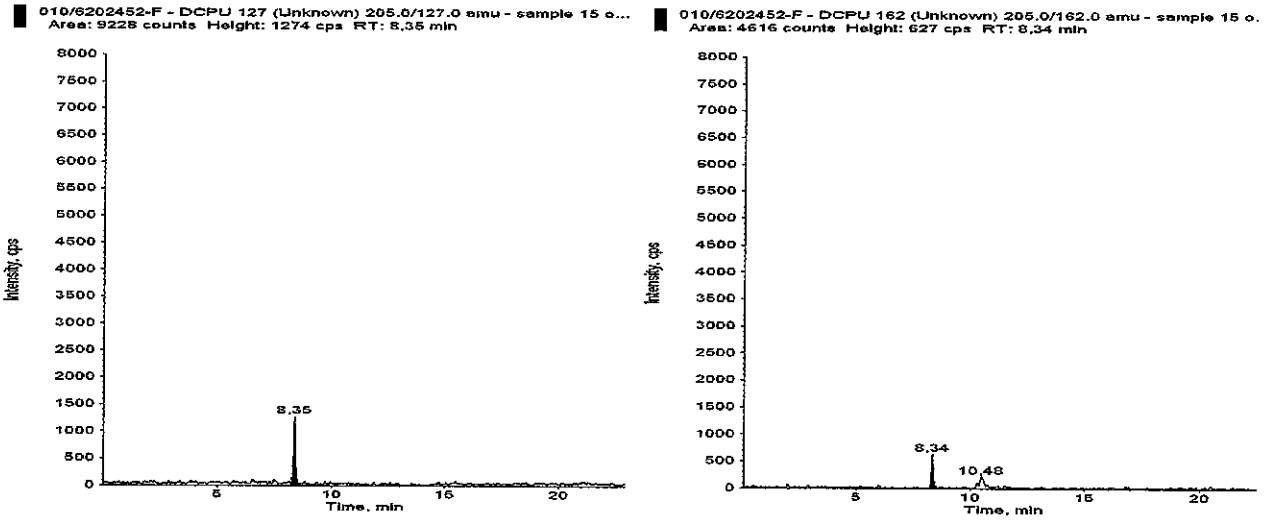


FIGURE 71 SURFACE WATER – DES. LINURON – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 mL

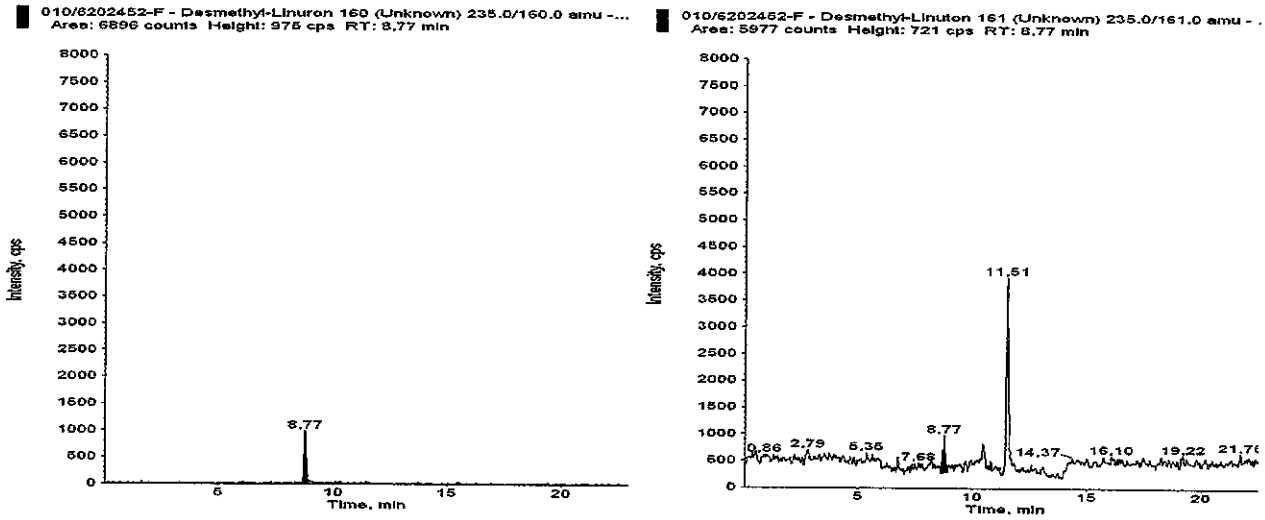


FIGURE 72 SURFACE WATER – MCPDMU – FORTIFIED SPECIMEN, 10-FOLD LOQ, FINAL VOLUME 10 mL