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Determination of DACT, ACET, Bromacil, Simazine, Hexazinone, Diuron,, Atrazine and Norflurazon in Soil by Liquid Chromatography-Mass Spectrometry

Scope: This method is for the determination of diaminochlorotriazine (DACT), deiospropylatrazine (ACET), bromacil, simazine, hexazinone, diuron, atrazine and norflurazon in soil using liquid chromatography-mass spectrometry (LC-MS). The reporting limit is 0.05 ppm for all compounds.

Principle: These analytes are extracted from soil with a mixture of hexane and acetone (1:1). After solvent evaporation, the residue is transferred with hexane and acetone (4:1) to a florisil Bond Elut. The analytes are eluted with hexane and acetone (4:1). The eluant is concentrated to approximate 0.1 mL and diluted to 2.0 ml with methanol and water (1:1). The extract of the sample is filtered through a 0.2 μ m Acrodisc into auto sampler vial for analysis. The analytes are isolated with C-8 column and detected with mass spectrometry.

Reagents:

Use residue grade solvent for sample extraction and ultra pure grade solvent and reagent for HPLC elution and Mass Spectrometry detection.

1. Diuron (CAS#330-54-1) 1.0 mg/mL, Hexazinone (CAS#51235-04-2) 1.0 mg/mL, DACT (CAS# 3397-62-4) 0.1 mg/mL, ACET (CAS#1007-28-9)1.0 mg/mL , Bromacil (CAS#314-40-9) 1.0 mg/m, Simazine (122-34-9) 0.25 mg/mL Atrazine (CAS #1912-24-9), and Norflurazon (CAS#27314-13-2)1.0 mg/mL, provide by the Standards Repository, Center for Analytical Chemistry, California Department of Food and Agriculture.
2. Methanol, pesticide residue grade and ultra pure grade, Burdick & Jackson
3. Hexane, pesticide residue grade
4. Acetone, pesticide residue grade
5. Water, ultra pure grade, Burdick & Jackson
6. Acetic acid, HPLC grade (Fisher #A35-500 or equivalent)
7. Acrodisc[®] 0.2 μ m, Gelman Laboratory, Cat # 09730191.
8. Florisil Mega Bond Elut[®], Varian Part Number 1225-6014.
9. Dry ice
10. Sodium sulfate, anhydrous
11. Sodium bicarbonate

Safety:

No known carcinogens were used in this method. However, for precaution, general laboratory safety procedures must be followed (e.g. wear safety glasses, gloves, use ventilation hood, etc...)

Equipment:

1. Blender, a quart size, stainless steel container, with Variac speed control(variable power transformer)
2. Aluminum weighing dish (57 mm) for determining moisture.
3. Balances, analytical and top load
4. Mason jar, quart size
5. Oven, 105 °C
6. Desiccator
7. Graduated cylinders,
8. Funnel
9. Glass wool
10. Boiling flask, flat bottomed, 24/24 joints, 250 mL
11. Rotary evaporator, Buchi, Model RE 111
12. Nylon Acrodisc, 0.2 um, Gelman
13. Graduated conical test tube, 15 mL, 5.0 mL calibrated
14. Nitrogen evaporator, Organomation, Model 112
15. Vortex mixer, Fisher Scientific, Model Vortex-Genie 2

Instrument: (see detail in operating parameters)

1. HPLC with autosampler and column oven
2. Mass spectrometer
3. Computer
4. C-18 HPLC column

Interference:

The detection of all analytes in this method are specific. Multiple factors were used to eliminate possible interferences. The factors were retention time, specific parent mass (M+1) and specific product ions,

	Precursor	product ions	Retention Time
Diuron	233,235	72	13.63
Hexazinone	254	171	12.56
DACT	146,148	110	6.27
ACET	174,176	132,146	9.06
Simazine	202	174,132,124	12.33
Bromacil	261,263	205,207	12.20
Atrazine	216	174,158	13.91
Norflurazon	304	284	13.97

No interference has been encountered

Standard Preparation:

Individual stock standards were obtained from the Standards Repository, CAC, CDFA. The concentrations were 1.00 mg/mL in methanol for ACET, bromacil, diuron, atrazine, hexazinone, and norflurazon. Due to the problem of low solubility, the stock solution concentrations were 0.1 mg/mL and 0.25 mg/mL in methanol for DACT and Simazine respectively. They were in ampules and stored in a freezer (less than -10°C). A 10 µg/mL mixed standard of all 8 compounds was prepared by mixing equal amount of the individual stock standards and diluted with methanol. This mixed standard was stored in a refrigerator (less than 5°C) and was used for spiking. Working standards were prepared by diluting the mixed standard with methanol and water (1:1) by volume and ratio. During this study we did not observe any problem of analytes stability in the standard solutions.

Sample Preservation and storage:

Check sample temperature upon arrival. Store all samples in a locked designated area in the walk-in freezer (less than -10 °C). Transport samples to a refrigerator (less than 5 °C) the night before sample preparation or extraction. Return to the freezer for storage immediately after subsample is taken.

Sample Preparation:

This procedure is for homogenizing the sample. Thaw the sample in a refrigerator overnight. Transfer a partial (about 200-300 grams) soil sample into a stainless steel blender jar. Add approximate 100-200 grams crushed dry ice. Blend the content at moderate speed until the sample appears sandy. Gradually add the remaining soil (usually about 600 grams) and add more dry ice to maintain the sandy texture. Make sure the sample is uniformly blended. Transfer the sample back to the original container, cover with aluminum foil and cap with lid loosely. Store the sample in a freezer over night to allow the dry ice to sublime. Remember to tightly cover the lid the following day. Use these prepared samples for moisture determination and sample extraction.

Moisture Determination:

1. Transport samples from freezer to refrigerator and allow them to thaw overnight. Prior to moisture determination and sample extraction, take the samples out from refrigerator and allow them to come to room temperature.
2. Weigh approximately 15 g of the homogenized sub sample into a preweighed aluminum weighing dish and record the wet weight. Clearly indicate whether the dish weight is included or not.
3. Place the weighing dish with sample into an oven at 105 °C for at least six hours. Remove the dish from oven and allow cooling in a desiccator. Weigh the dried sample and record the Weight.

Sample Extraction:

1. Weigh out 25 g of the homogenized sample into a one-pint wide mouth Mason jar. (For QC samples, spike at this step, mix and set for 30 minutes before continuing).
2. Add 5 grams sodium bicarbonate to the sample and mix them.

3. Add 100 mL 50:50 hexane in acetone. Sonicate for 45 minutes. Swirl the sample every 15 minutes. Decant the organic solvent through a funnel containing glass wool and 20 g of anhydrous sodium sulfate into a 500 mL flat bottomed boiling flask. Use a minimum amount of glass wool. It is just for supporting the sodium sulfate.
4. Repeat step 3.
5. Rinse with 40 mL 50:50 hexane in acetone through the sodium sulfate.
6. Evaporate the extract to about 2 mL on a rotary evaporator at approx. 40 °C water bath and 15 mm Hg vacuum
7. Condition a Florisil Bond Elute cartridge with 8 mL of 20% hexane in acetone. Switch the vacuum manifold to collect position. Transfer the residue from the flask to the conditioned cartridge. Wash the flask with 5 mL 20% hexane in acetone and transfer to the conditioned cartridge. Repeat the wash two more time.
8. Evaporate the combined eluant to about 0.1 mL using a N-evap at 40 °C. Bring to a final volume of 2.0 mL with methanol and water (1:1). Mix well and filter through a 0.2 μ Acrodisc into two autosamplers.
9. Analyze the sample extract on a HPLC-MS system.

Equipment Conditions:

HPLC System and Operating Parameters

Instrument: Waters model 2690 HPLC, gradient pump, auto sampler, column heater and remote control through Finnigan Xcalibur system

Detector: Finnigan LCQ Deca Mass spectrometer

Column: Agilent Zorbax SB-C8 3.5μm 4.6x 150mm

Precolumn: Phenomex C-8 5 mm L x 2.0 mm ID cartridge (AJO-4286)

Column Temperature: 40 °C

Solvent: Gradient Program,

Solvent A: 0.1% acetic acid in methanol

Solvent B: 0.1% acetic acid in ultra pure water

Time (min)	Flow (ml/min)	A (%)	B (%)
0.00	0.6	10	90
1.00	0.6	10	90
8.0	0.6	60	40
15.0	0.6	80	20
18.0	0.6	10	90
20.0	0.6	10	90

Total run time 20 minutes

Flow rate: 0.6 mL / min

Injection volume: 10 μL

Retention time: listed in previous section

Note: An alternative C-8 or C-18 column will probably work. You may also vary the mobile phase percentage at your convenience.

Mass Spectrometry System and Operating Parameters: see the Table 1

Finnigan LCQ Deca, ion trap mass spectrometer
 Instrument control and data handling: Gateway computer model E-4200
 Software: Xcalibur Version 1 SR1

Tune files: see the Table 2

Instrument Calibration:

A 5 level standards were run before and after each sample set. The concentration of working standards were 0.2, 0.4, 0.6, 0.8 and 1.0 ng/μL. The standard curve had correlation coefficient (R²) = 0.990 or better.

Analysis:

Build up a sequence. Inject the first standard at least twice to condition the instrument. Log-in the correct dilution factors. The sequence is in the order of standards, blank, spikes, 10 or less samples and standards, then repeat.

Calculations:

Report the percent moisture on a **dry weight** basis.

$$\% \text{ moisture} = (\text{Wet weight} - \text{Dry weight}) / \text{Dry weight} \times 100$$

Calculate the concentration of chemical(s) of a sample as follows:

$$\text{ppm} = \frac{(\text{peak area. sample}) (\text{std. conc. } \mu\text{g/mL}) (\text{std. vol. injected}) (\text{final vol. sample, mL})}{(\text{peak area. std.}) (\text{sample vol. injected}) (\text{sample wt., g})} \times \text{dilution Factor}$$

Using the program of LCQuan software in Xcalibur for actual calculation

In general, std vol. Injected = sample vol injected.

final volume = 2.0 mL

sample wt. = 25 g.

The ions used for quantitation for each compound are listed in the following table

Compound name	Ions
DACT	110
DACT (unfragmented)	146,148
ACET	132,146
ACET (unfragmented)	174,176
Simazine	174,132,124
Bromacil	205,207

Hexazinone	171
Diuron	72
Atrazine	174,158
Norflurazon	284

Method Performance:

Method Detection Limit:

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably in either a sample or blank. To determine the MDL, each of the 7 samples containing 25.0 g of background soil were spiked separately with 0.06 ppm of the eight compounds. These spiked samples along with a blank were extracted and analyzed using the described method. The standard deviation derived from the 7 spiked samples was used to calculate the MDL using the following equation:

$$MDL = t S$$

where:

t is the Student 't' value for the 99% confidence level with n-1 degrees of freedom (n-1, 1 - α = 0.99). **n** represents the number of replicates.

S denotes the standard deviation obtained from replicate analyses.

The results for the standard deviations and MDLs are in Table 3

Reporting Limit:

Report Limit (RL) refers to the level above which quantitative results may be obtained usually 1-5 times the MDL

Spiking solution and spiking volume:

MDL, method validation and QC spikes are made by spiking into 25.0 g of background soil With the combination standards

The concentration of combination standard for spiking is 10.0 ng/μL for all compounds. The volumes spiked are listed in the following table.

	Sample Size (grams)	Volume Added (μL)	Analyte Spiked (μg)	Equivalent to (ppm)
MDL	25	150	1.5	0.06
Validation level 1	25	250	2.5	0.10
Validation level 2	25	1250	12.5	0.50
Validation level 3	25	2500	25.0	1.0
Validation level 4	25	5000	50.0	2.0
Set QC	25	250	2.5	0.1

Method Validation Data: This analytical method is validated using five sets of spike samples. The recovery data for all compounds are listed in See Table 4

Acceptance Criteria:


1. All samples must be injected at least two times. The standard curves at the beginning and end of each sample set should not have a percent change greater than 20%. The % change in response was calculated as follows:
$$\% \text{ Change in response} = \frac{\text{absolute value of [slope of (STD curve before - STD curve after)]}}{\text{STD curve before}} \times 100$$
2. The sample results were calculated based on the average of two adjacent calibration curves using Xcalibur software. When the difference between the two injections was less than 15%, either result can be reported. Additional injections were required if the differences were greater than 15%.

Discussion:

This method provides very good accuracy and precision, as measured by the average recovery at all spiking levels for all compounds. DACT and ACET are analyzed by two MS methods, fragmented and unfragmented, concurrently. The results are in extremely good agreement. The Q-value in the trap for the fragmentation of DACT and ACET are set at 0.400. The default for this value is 0.25, which causes the response of the product ions to be irregular.

Reference:

Written By: Paul Lee


Title: Agricultural Chemist III

Approved By: Catherine Cooper



Title: Agricultural Chemist III
Supervisor

Table 1 Mass Spectrometer Method Parameters

	DACT	DACT	ACET	ACET	Bromacil	Simazine	Hexazinone	Diuron	Diuron	Atrazine	Norflurazon
Duration (min)	8.14	8.14	2.91	2.91	2.12	2.12	2.12	0.58	0.58	2.22	2.22
Retention time	6.29	6.29	9.06	9.06	12.2	12.33	12.56	13.63	13.63	13.91	13.97
# scan event	2	2	2	2	3	3	3	2	2	2	2
Segment 1											
Tune method	1-04-02 146										
Scan Events											
ms/ms	147	147									
mass range	60-160	50-160									
Amp	30.0%	20.0%									
Q-value	0.400	0.250									
ActivationTime	100	30									
IsoW	4	4									
Segment 2											
Tune method			1-04-02 146								
Scan events											
ms/ms			175	175							
mass range			75-180	50-180							
Amp			32.0%	20.0%							
Q-value			0.400	0.250							
ActivationTime			100	30							
IsoW			4	4							
Segment 3											
Tune method					1-04-02 146						
Scan events											
ms/ms					262	202	252				
mass range					70-280	80-220	65-260				
Amp					22.00%	32.00%	26.00%				
Q-value					0.250	0.250	0.250				
ActivationTime					30	30	30				
IsoW					4	4	4				
Segment 4											
Tune method								-05-02 233-72 1-40			
Scan events											
ms/ms								234	234		
mass range								60-300	60-240		
Amp								10	30		
Q-value								0.250	0.240		
ActivationTime								30	30		
IsoW								4	4		
Segment 5											
Tune method										1-04-02 146	
Scan events											
ms/ms										216	304
mass range										55-300	80-320
Amp										30	32
Q-value										0.25	0.25

Table 2 Tune methods

Tune method names	1-04-02 146	2-5-02 233-72 1-400
Polarity	Positive	Positive
Capillary Temp (C):	275	275
APCI Vaporizer Temp (C):	500	500
Ion Time (ms):	5	5
Sheath Gas Flow (l):	38	38
Aux Gas Flow (l):	5	5
Source Type:	APCI	APCI
Injection Waveforms:	Off	Off
AGC:	On	On
POSITIVE POLARITY		
Source Voltage (kV):	6	6
Source Current (uA):	5	5
Capillary Voltage (V):	9	14
Tube Lens Offset (V):	5	10
Octapole RF Amplifier (Vp-)	400	400
Octapole 1 Offset (V):	-2.25	-8.75
Octapole 2 Offset (V):	-8	-12
Entrance Lens (V):	-44	-30
InterOctapole Lens Voltage	-56	-48
Trap DC Offset Voltage (V)	-10	-10
Zoom Micro Scans:	5	5
Zoom AGC Target:	20000000	20000000
Zoom Max Ion Time (ms):	50	50
Full Micro Scans:	3	3
Full AGC Target:	50000000	50000000
Full Max Ion Time (ms):	300	300
SIM Micro Scans:	3	3
SIM AGC Target:	20000000	20000000
SIM Max Ion Time (ms):	100	100
MSn Micro Scans:	1	1
MSn AGC Target:	20000000	20000000
MSn Max Ion Time (ms):	1000	400

Table 3. Determination of MDL

Sample #	Injection	DACT		DACT (Unfragmented)		ACET		ACET (Unfragmented)	
		Spiked (ppm)	Found (ppm)	Spiked (ppm)	Found (ppm)	Spiked (ppm)	Found (ppm)	Spiked (ppm)	Found (ppm)
1	1	0.060	0.033	0.060	0.033	0.060	0.035	0.060	0.035
1	2	0.060	0.032	0.060	0.033	0.060	0.034	0.060	0.035
2	1	0.060	0.044	0.060	0.046	0.060	0.053	0.060	0.051
2	2	0.060	0.046	0.060	0.047	0.060	0.051	0.060	0.049
3	1	0.060	0.047	0.060	0.047	0.060	0.053	0.060	0.053
3	2	0.060	0.047	0.060	0.047	0.060	0.049	0.060	0.052
4	1	0.060	0.043	0.060	0.044	0.060	0.050	0.060	0.051
4	2	0.060	0.045	0.060	0.044	0.060	0.048	0.060	0.048
5	1	0.060	0.045	0.060	0.044	0.060	0.051	0.060	0.052
5	2	0.060	0.044	0.060	0.044	0.060	0.052	0.060	0.050
6	1	0.060	0.047	0.060	0.048	0.060	0.054	0.060	0.054
6	2	0.060	0.048	0.060	0.049	0.060	0.053	0.060	0.050
7	1	0.060	0.047	0.060	0.049	0.060	0.051	0.060	0.053
7	2	0.060	0.047	0.060	0.047	0.060	0.053	0.060	0.053
Average1			0.044		0.045		0.050		0.050
STDEV1			0.005		0.005		0.007		0.007
MDL1			0.016		0.017		0.021		0.021
Average2			0.044		0.044		0.049		0.048
STDEV2			0.006		0.005		0.007		0.006
MDL2			0.018		0.017		0.021		0.019

Sample #	Injection	Bromacil		Simazine		Hexazinone		Diuron	
		Spiked (ppm)	Found (ppm)	Spiked (ppm)	Found (ppm)	Spiked (ppm)	Found (ppm)	Spiked (ppm)	Found (ppm)
1	1	0.060	0.033	0.060	0.031	0.060	0.037	0.060	0.027
1	2	0.060	0.035	0.060	0.032	0.060	0.037	0.060	0.029
2	1	0.060	0.051	0.060	0.050	0.060	0.050	0.060	0.049
2	2	0.060	0.049	0.060	0.049	0.060	0.049	0.060	0.056
3	1	0.060	0.055	0.060	0.054	0.060	0.049	0.060	0.053
3	2	0.060	0.050	0.060	0.053	0.060	0.052	0.060	0.049
4	1	0.060	0.046	0.060	0.045	0.060	0.047	0.060	0.052
4	2	0.060	0.047	0.060	0.048	0.060	0.042	0.060	0.052
5	1	0.060	0.051	0.060	0.051	0.060	0.040	0.060	0.044
5	2	0.060	0.047	0.060	0.052	0.060	0.047	0.060	0.050
6	1	0.060	0.053	0.060	0.054	0.060	0.050	0.060	0.045
6	2	0.060	0.053	0.060	0.053	0.060	0.058	0.060	0.046
7	1	0.060	0.049	0.060	0.053	0.060	0.050	0.060	0.048
7	2	0.060	0.050	0.060	0.051	0.060	0.051	0.060	0.059
Average1			0.048		0.048		0.046		0.046
STDEV1			0.007		0.008		0.005		0.009
MDL1			0.023		0.026		0.016		0.028
Average2			0.047		0.048		0.048		0.049
STDEV2			0.006		0.007		0.007		0.010
MDL2			0.018		0.023		0.021		0.030

Sample #	Injection	Atrazine		Norflurazon	
		Spiked (ppm)	Found (ppm)	Spiked (ppm)	Found (ppm)
1	1	0.060	0.029	0.060	0.032
1	2	0.060	0.032	0.060	0.034
2	1	0.060	0.049	0.060	0.053
2	2	0.060	0.050	0.060	0.050
3	1	0.060	0.050	0.060	0.052
3	2	0.060	0.050	0.060	0.055
4	1	0.060	0.048	0.060	0.048
4	2	0.060	0.046	0.060	0.049
5	1	0.060	0.045	0.060	0.052
5	2	0.060	0.048	0.060	0.048
6	1	0.060	0.053	0.060	0.058
6	2	0.060	0.049	0.060	0.052
7	1	0.060	0.049	0.060	0.050
7	2	0.060	0.052	0.060	0.056
Average1			0.046		0.049
STDEV1			0.008		0.008
MDL1			0.025		0.026
Average2			0.047		0.049
STDEV2			0.007		0.007
MDL2			0.021		0.023

Table 4 Method Validation Recovery Data

SET1	DACT (fragmented)			DACT (not fragmented)			ACET (fragmented)		
	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.080	80%	0.100	0.083	83%	0.100	0.087	87%
inj 2	0.100	0.088	88%	0.100	0.083	83%	0.100	0.090	90%
inj 1	0.500	0.414	83%	0.500	0.420	84%	0.500	0.447	89%
inj 2	0.500	0.416	83%	0.500	0.408	82%	0.500	0.478	96%
inj 1	1.000	0.740	74%	1.000	0.801	80%	1.000	0.883	88%
inj 2	1.000	0.840	84%	1.000	0.787	79%	1.000	0.904	90%
inj 1	2.000	1.541	77%	2.000	1.605	80%	2.000	1.700	85%
inj 2	2.000	1.571	79%	2.000	1.577	79%	2.000	1.753	88%
SET2	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.084	84%	0.100	0.084	84%	0.100	0.093	93%
inj 2	0.100	0.080	80%	0.100	0.086	86%	0.100	0.098	98%
inj 1	0.500	0.390	78%	0.500	0.395	79%	0.500	0.473	95%
inj 2	0.500	0.380	76%	0.500	0.407	81%	0.500	0.506	101%
inj 1	1.000	0.780	78%	1.000	0.780	78%	1.000	0.928	93%
inj 2	1.000	0.802	80%	1.000	0.818	82%	1.000	0.925	92%
inj 1	2.000	1.596	80%	2.000	1.593	80%	2.000	1.828	91%
inj 2	2.000	1.633	82%	2.000	1.606	80%	2.000	1.867	93%
SET3	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.095	95%	0.100	0.092	92%	0.100	0.093	93%
inj 2	0.100	0.099	99%	0.100	0.093	93%	0.100	0.095	95%
inj 1	0.500	0.480	96%	0.500	0.462	92%	0.500	0.475	95%
inj 2	0.500	0.526	105%	0.500	0.483	97%	0.500	0.471	94%
inj 1	1.000	0.883	88%	1.000	0.847	85%	1.000	0.859	86%
inj 2	1.000	0.923	92%	1.000	0.853	85%	1.000	0.858	86%
inj 1	2.000	1.729	86%	2.000	1.686	84%	2.000	1.639	82%
inj 2	2.000	1.836	92%	2.000	1.759	88%	2.000	1.760	88%
SET4	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.079	79%	0.100	0.080	80%	0.100	0.091	91%
inj 2	0.100	0.081	81%	0.100	0.078	78%	0.100	0.092	92%
inj 1	0.500	0.412	82%	0.500	0.393	79%	0.500	0.466	93%
inj 2	0.500	0.392	78%	0.500	0.396	79%	0.500	0.439	88%
inj 1	1.000	0.815	82%	1.000	0.788	79%	1.000	0.916	92%
inj 2	1.000	0.749	75%	1.000	0.778	78%	1.000	0.867	87%
inj 1	2.000	1.574	79%	2.000	1.604	80%	2.000	1.823	91%
inj 2	2.000	1.613	81%	2.000	1.591	80%	2.000	1.865	93%
Set5 (6)	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.078	78%	0.100	0.075	75%	0.100	0.093	93%
inj 2	0.100	0.081	81%	0.100	0.078	78%	0.100	0.096	96%
inj 1	0.500	0.409	82%	0.500	0.378	76%	0.500	0.444	89%
inj 2	0.500	0.400	80%	0.500	0.392	78%	0.500	0.453	91%
inj 1	1.000	0.778	78%	1.000	0.776	78%	1.000	0.919	92%
inj 2	1.000	0.832	83%	1.000	0.817	82%	1.000	0.932	93%
inj 1	2.000	1.588	79%	2.000	1.599	80%	2.000	1.648	82%
inj 2	2.000	1.694	85%	2.000	1.651	83%	2.000	1.809	90%
AVERAGE			83.1%			81.7%			90.9%
STDEV			7.06%			4.98%			3.97%
Average1			81.9%			81.4%			90.1%
Stdev1			5.74%			4.60%			3.84%
Average2			84.2%			82.5%			92.1%
Stdev2			7.66%			5.01%			3.94%

	ACET (not fragmented)			Bromacil			Simazine			
SET1	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery	
	inj 1	0.100	0.090	90%	0.100	0.091	91%	0.100	0.065	65%
	inj 2	0.100	0.088	88%	0.100	0.091	91%	0.100	0.064	64%
	inj 1	0.500	0.474	95%	0.500	0.457	91%	0.500	0.325	65%
	inj 2	0.500	0.464	93%	0.500	0.422	84%	0.500	0.337	67%
	inj 1	1.000	0.895	90%	1.000	0.887	89%	1.000	0.652	65%
	inj 2	1.000	0.890	89%	1.000	0.849	85%	1.000	0.674	67%
	inj 1	2.000	1.643	82%	2.000	1.747	87%	2.000	1.691	85%
	inj 2	2.000	1.775	89%	2.000	1.676	84%	2.000	1.574	79%
SET2	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery	
	inj 1	0.100	0.093	93%	0.100	0.098	98%	0.100	0.090	90%
	inj 2	0.100	0.096	96%	0.100	0.093	93%	0.100	0.097	97%
	inj 1	0.500	0.466	93%	0.500	0.470	94%	0.500	0.452	90%
	inj 2	0.500	0.472	94%	0.500	0.491	98%	0.500	0.463	93%
	inj 1	1.000	0.923	92%	1.000	0.852	85%	1.000	0.855	85%
	inj 2	1.000	0.917	92%	1.000	0.857	86%	1.000	0.908	91%
	inj 1	2.000	1.727	86%	2.000	1.827	91%	2.000	1.769	88%
	inj 2	2.000	1.888	94%	2.000	1.963	98%	2.000	1.792	90%
SET3	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery	
	inj 1	0.100	0.092	92%	0.100	0.081	81%	0.100	0.092	92%
	inj 2	0.100	0.093	93%	0.100	0.088	88%	0.100	0.095	95%
	inj 1	0.500	0.462	92%	0.500	0.425	85%	0.500	0.441	88%
	inj 2	0.500	0.483	97%	0.500	0.463	93%	0.500	0.484	97%
	inj 1	1.000	0.847	85%	1.000	0.688	69%	1.000	0.756	76%
	inj 2	1.000	0.853	85%	1.000	0.833	83%	1.000	0.786	79%
	inj 1	2.000	1.686	84%	2.000	1.629	81%	2.000	1.498	75%
	inj 2	2.000	1.759	88%	2.000	1.658	83%	2.000	1.575	79%
SET4	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery	
	inj 1	0.100	0.089	89%	0.100	0.090	90%	0.100	0.095	95%
	inj 2	0.100	0.091	91%	0.100	0.088	88%	0.100	0.096	96%
	inj 1	0.500	0.460	92%	0.500	0.482	96%	0.500	0.456	91%
	inj 2	0.500	0.467	93%	0.500	0.496	99%	0.500	0.467	93%
	inj 1	1.000	0.875	88%	1.000	0.885	89%	1.000	0.838	84%
	inj 2	1.000	0.881	88%	1.000	0.870	87%	1.000	0.856	86%
	inj 1	2.000	1.866	93%	2.000	1.888	94%	2.000	1.659	83%
	inj 2	2.000	1.798	90%	2.000	1.981	99%	2.000	1.795	90%
Set5 (6)	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery	
	inj 1	0.100	0.091	91%	0.100	0.086	86%	0.100	0.090	90%
	inj 2	0.100	0.094	94%	0.100	0.096	96%	0.100	0.099	99%
	inj 1	0.500	0.452	90%	0.500	0.487	97%	0.500	0.420	84%
	inj 2	0.500	0.483	97%	0.500	0.446	89%	0.500	0.470	94%
	inj 1	1.000	0.900	90%	1.000	0.898	90%	1.000	0.876	88%
	inj 2	1.000	0.915	91%	1.000	0.903	90%	1.000	0.894	89%
	inj 1	2.000	1.771	89%	2.000	1.699	85%	2.000	1.652	83%
	inj 2	2.000	1.796	90%	2.000	1.747	87%	2.000	1.797	90%
AVERAGE			90.6%			88.9%			85.6%	
STDEV			3.39%			6.25%			9.08%	
Average1			89.8%			88.6%			83.1%	
Stdev1			3.40%			6.78%			9.27%	
Average2			91.6%			90.1%			86.7%	
Stdev2			3.21%			5.53%			10.63%	

	Hexazinone			Diuron			Atrazine		
SET1	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.076	76%	0.100	0.079	79%	0.100	0.096	96%
inj 2	0.100	0.073	73%	0.100	0.090	90%	0.100	0.096	96%
inj 1	0.500	0.440	88%	0.500	0.375	75%	0.500	0.415	83%
inj 2	0.500	0.368	74%	0.500	0.368	74%	0.500	0.449	90%
inj 1	1.000	0.749	75%	1.000	0.929	93%	1.000	0.858	86%
inj 2	1.000	0.774	77%	1.000	0.753	75%	1.000	0.847	85%
inj 1	2.000	1.683	84%	2.000	1.651	83%	2.000	1.834	92%
inj 2	2.000	1.549	77%	2.000	1.476	74%	2.000	1.807	90%
SET2	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.086	86%	0.100	0.088	88%	0.100	0.096	96%
inj 2	0.100	0.093	93%	0.100	0.097	97%	0.100	0.101	101%
inj 1	0.500	0.458	92%	0.500	0.420	84%	0.500	0.483	97%
inj 2	0.500	0.441	88%	0.500	0.444	89%	0.500	0.494	99%
inj 1	1.000	0.813	81%	1.000	0.897	90%	1.000	0.887	89%
inj 2	1.000	0.827	83%	1.000	0.949	95%	1.000	0.997	100%
inj 1	2.000	1.776	89%	2.000	1.542	77%	2.000	1.866	93%
inj 2	2.000	1.667	83%	2.000	1.782	89%	2.000	1.859	93%
SET3	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.087	87%	0.100	0.091	91%	0.100	0.095	95%
inj 2	0.100	0.086	86%	0.100	0.083	83%	0.100	0.099	99%
inj 1	0.500	0.457	91%	0.500	0.442	88%	0.500	0.480	96%
inj 2	0.500	0.464	93%	0.500	0.469	94%	0.500	0.526	105%
inj 1	1.000	0.834	83%	1.000	0.857	86%	1.000	0.883	88%
inj 2	1.000	0.890	89%	1.000	0.856	86%	1.000	0.923	92%
inj 1	2.000	1.638	82%	2.000	1.633	82%	2.000	1.729	86%
inj 2	2.000	1.891	95%	2.000	1.996	100%	2.000	1.836	92%
SET4	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.085	85%	0.100	0.089	89%	0.100	0.093	93%
inj 2	0.100	0.091	91%	0.100	0.101	101%	0.100	0.093	93%
inj 1	0.500	0.424	85%	0.500	0.453	91%	0.500	0.472	94%
inj 2	0.500	0.423	85%	0.500	0.383	77%	0.500	0.483	97%
inj 1	1.000	0.794	79%	1.000	0.900	90%	1.000	0.923	92%
inj 2	1.000	0.862	86%	1.000	0.783	78%	1.000	0.921	92%
inj 1	2.000	1.744	87%	2.000	1.779	89%	2.000	1.862	93%
inj 2	2.000	1.698	85%	2.000	1.989	99%	2.000	1.777	89%
Set5 (6)	Spiked	Found	% recovery	Spiked	Found	% recovery	Spiked	Found	% recovery
inj 1	0.100	0.082	82%	0.100	0.089	89%	0.100	0.093	93%
inj 2	0.100	0.096	96%	0.100	0.091	91%	0.100	0.096	96%
inj 1	0.500	0.445	89%	0.500	0.434	87%	0.500	0.441	88%
inj 2	0.500	0.438	88%	0.500	0.465	93%	0.500	0.476	95%
inj 1	1.000	0.800	80%	1.000	0.856	86%	1.000	0.915	91%
inj 2	1.000	0.924	92%	1.000	0.918	92%	1.000	0.938	94%
inj 1	2.000	1.702	85%	2.000	1.680	84%	2.000	1.717	86%
inj 2	2.000	1.783	89%	2.000	1.675	84%	2.000	1.768	88%
AVERAGE			85.6%			86.8%			92.3%
STDEV			5.27%			7.19%			4.62%
Average1			84.3%			86%			91.4%
Stdev1			4.61%			4.89%			4.07%
Average2			86.1%			88.0%			94.3%
Stdev2			6.64%			8.87%			4.91%

Norflurazon

SET1	Spiked	Found	% recovery
	0.100	0.080	80%
	0.100	0.088	88%
	0.500	0.414	83%
	0.500	0.416	83%
	1.000	0.740	74%
	1.000	0.840	84%
	2.000	1.822	91%
	2.000	1.836	92%

SET2	Spiked	Found	% recovery
	0.100	0.095	95%
	0.100	0.101	101%
	0.500	0.483	97%
	0.500	0.480	96%
	1.000	0.935	94%
	1.000	0.991	99%
	2.000	1.791	90%
	2.000	1.992	100%

SET3	Spiked	Found	% recovery
	0.100	0.089	89%
	0.100	0.093	93%
	0.500	0.472	94%
	0.500	0.497	99%
	1.000	0.909	91%
	1.000	0.913	91%
	2.000	1.805	90%
	2.000	1.851	93%

SET4	Spiked	Found	% recovery
	0.100	0.100	100%
	0.100	0.097	97%
	0.500	0.485	97%
	0.500	0.486	97%
	1.000	0.945	95%
	1.000	0.939	94%
	2.000	1.841	92%
	2.000	1.927	96%

SET5	Spiked	Found	% recovery
	0.100	0.091	91%
	0.100	0.098	98%
	0.500	0.455	91%
	0.500	0.468	94%
	1.000	0.878	88%
	1.000	0.930	93%
	2.000	1.765	88%
	2.000	1.853	93%

AVERAGE	92.4%
STDEV	5.37%

Average1	90.5%
Stdev1	6.03%

Average2	94.0%
Stdev2	4.87%