

Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pesticide Name: Clodinafop-Propargyl

MRID #: 446461-01

Matrix: Soil

Analysis: GC/MS

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VOLUME 2 OF 4 OF SUBMISSION

CGA-184927 and CGA-193469

TITLE

Method of Analysis for the Determination of CGA 184927 and the
Acid Metabolite CGA 193469 by GC/MS

DATA REQUIREMENT

Supplement to EPA Guideline No. 164-1

AUTHOR

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COMPLETION DATE

March 11, 1998

PERFORMING LABORATORY

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LABORATORY PROJECT IDENTIFICATION

ETL Method No. MS 147.00
Novartis Number 321-98

SUBMITTER/SPONSOR

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VOLUME 1 OF 1 OF STUDY

STATEMENT OF NO DATA CONFIDENTIALITY CLAIM

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COMPANY AGENT: Karen Stumpf

TITLE: Senior Regulatory Manager

SIGNATURE:

Karen Stumpf

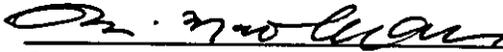
DATE:

8/24/98

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The document in this submission is an analytical method and is not considered a final report because validation of the method is not included. Therefore, certification of compliance with USEPA Good Laboratory Practice Standards Standards, 40 CFR 160, is not required.


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ANALYTICAL METHOD MS 147.00
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METHOD TITLE: Method of Analysis for the Determination of CGA 184927
and the acid metabolite CGA 193469 by GC/MS

EFFECTIVE DATE: January 1993

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OF ORIGINAL

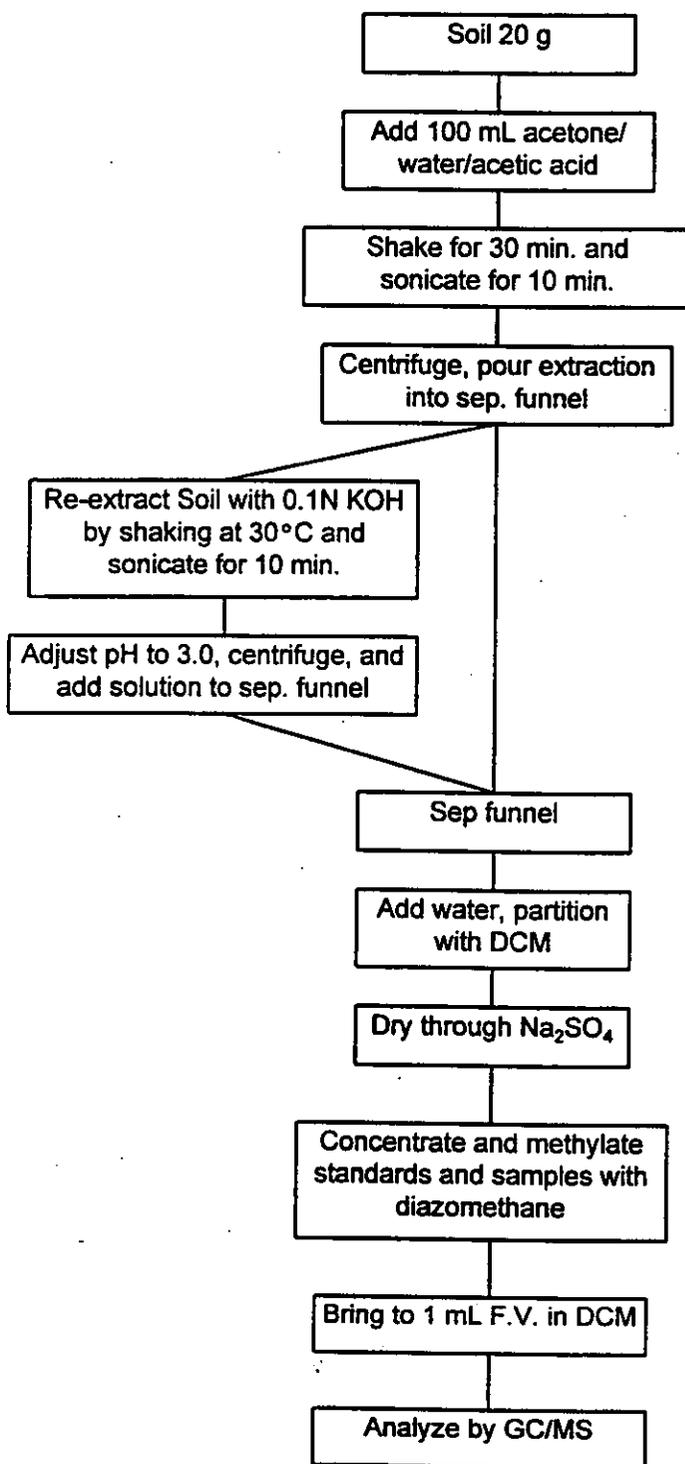
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TOTAL NO. PAGES: 37

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SUMMARY FLOWCHART OF ANALYTICAL METHOD



1.0 INTRODUCTION

1.1 Scope

This method sets forth the procedure for determining the residues of CGA 184927 and CGA 193469 in soil. The method is based on an in-house method developed at Enviro-Test Laboratories (Edmonton, Alberta).

1.2 Principle

An analytical method is described for the determination of residues of CGA 184927 and CGA 193469 in soil. Residues of target analytes are extracted from soil by shaking and sonication using acidic acetone and basic aqueous solutions. The acid metabolite CGA 193469 is methylated with diazomethane and residue analysis is done by GC/MS on a DB-1701 column. Quantitation of results is based on a comparison of peak areas with those of known standards or quantitation can be done using a linearity curve.

1.3 Method Limits

The limit of detection (LOD) and minimum limit of quantitation (LOQ) was different for each compound. They are listed below and are based on a 20 g sample and a 1.0 final volume.

Compound	LOD (ppm)	LOQ (ppm)
CGA 184927	0.010	0.030
CGA 193469	0.0030	0.010

2.0 MATERIALS

2.1 Reagents/Solvents (Equivalent/better grade reagents/solvents may be substituted.)

Acetone - Pesticide grade (B & J)

Acetic Acid - (BDH, AnalaR Analytical Reagent)

Benzyl Chloroformate - Silanizing Reagent (Aldrich, Technical grade)

Diazomethane - (PSOP3.01 - Appendix 2)

2.1 Reagents/Solvents cont'd (Equivalent/better grade reagents/solvents may be substituted.)

Dichloromethane (DCM) - (OmniSolv®)

Potassium Hydroxide Pellets - (Fisher Scientific)

Sulfuric Acid - (Analar Analytical Reagent)

Sodium Sulphate - (BDH, Analytical Reagent)(GSOP10.01 - Appendix 2)

Acid washed: Bake at 400°C for at least 4 hours, cool, transfer to a 1 L flask and add enough ether to cover a ~2.0 mL of concentrated H₂SO₄.

Mix, remove ether and dry at room temperature.

Water, deionized - Millipore Purification System

2.2 Equipment and Supplies (Equivalent equipment may be substituted.)

Bottles, centrifuge, polypropylene, 250 mL - (Baxter/CanLab)

Centrifuge - Sorvall®, RC2-B with 250 mL rotor head, (DuPont Instruments)

Flasks, round bottom - 500 mL

Funnels, separatory - 250 mL and 500 mL

Funnels, polypropylene - (Baxter/CanLab)

Incubator Shaker, Controlled Environment - (New Brunswick Scientific Co.Inc.)

N-Evap-Organomation - Model 111 (Meyer)

pH Paper, wide range - Colorphast® Range 0-14 (Chemonics Scientific)

Rotary Evaporator - Janke & Hunkel (IKA Labortechnik, Cincinnati, OH 45241)

Sonicator, Solid State/Ultrasonic FS-28 - (Fisher Scientific)

2.3 Solutions

2.3.1 Water/Acetone/Acetic acid (20:79:1) Percent by volume ie. Mix 200 mL water, 790 mL acetone and 10 mL of acetic acid.

2.3.2 0.1N KOH: Weigh out 8.4 g of KOH pellets and dissolve by bringing it to 1.5 L with water.

2.3.3 6N H₂SO₄: Take 160 mL of concentrated H₂SO₄ and bring to 1 L with water.

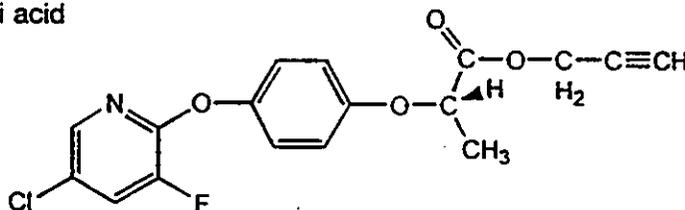
2.4 Analytical Standard and Chemical Structure:

CGA 184927

Chemical Name: 2-[4-(5-Chloro-3-fluoro-
pyridin-2-yloxy)-phenoxy]-propioni acid
prop-2-ynyl ester

Lot #: OP111005

% Purity: 97.2%

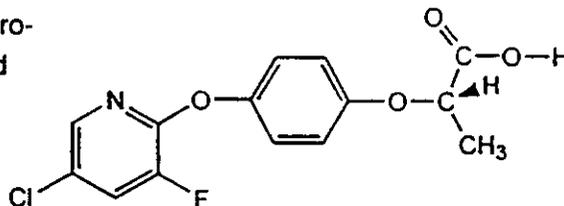
Source: Novartis Crop
Protection

CGA 193469

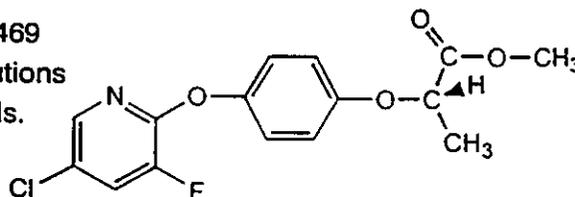
Chemical Name: 2-[4-(5-Chloro-3-fluoro-
pyridin-2-yloxy)-phenoxy]-propioni acid

Lot #: SC 3944\B

% Purity: 99.4%

Source: Novartis Crop
Protection

Methyl ester of CGA 193469

A 10 ppm procedural methylated CGA 193469
standard is prepared with each set and dilutions
of this are done for the calibration standards.**3.0 FORTIFICATION AND CALIBRATION STANDARD SOLUTIONS****3.1 Preparation**

All the standard solutions must be stored in glass at or below 10°C when not in use. Solutions should be allowed to warm to room temperature prior to use. The following is an example procedure for preparing a standard solution. Alternate or additional standards of appropriate weight and volume may be prepared as needed. The "≈" symbol indicates approximately.

3.1 Preparation cont'd

- 3.1.1 Weigh ~ 0.010 g (corrected for purity) and record the exact amount of the analyte of interest and then place into a 10 mL volumetric flask and dilute to the mark with acetonitrile. Cap and mix by inversion. The concentration of these stock standards is ~1000 µg/mL.
- 3.1.2 For the preparation of calibration and fortification standards transfer 10 mL of the ~1000 µg/mL standard via volumetric class "A" pipettes, to a 100 mL volumetric flask. Dilute to mark with acetonitrile. Cap and mix by inversion. The concentration of this standard is ~100 µg/mL. Prepare a similar fortification standard of 10 ppm by serial dilution in DCM.
- 3.1.3 Mixed Calibration Standards of the methyl ester of CGA 193469 and CGA 184927 are prepared by combining 200 µL of the 100 ppm fortification standards of CGA 193469 and CGA 184927 with 1 mL of diazomethane. The reaction is allowed to react for 5 minutes, ensuring the yellow color persists. If not, 0.5 mL of diazomethane is added. The diazomethane is then evaporated using an N-evaporator in the fumehood to ~ 0.5 mL then made up to a 5 mL final volume in DCM. This give a concentration of 4 ppm. Other calibration standards (eg. at 2.0, 1.0 and 0.03 ppm) are made by serial dilution in DCM.

3.2 Stability

To evaluate the stability, the following formula has been used:

$$\% \text{ Stability} = \left(1 - \frac{\text{old standard solution}}{\text{new standard solution}} \right) \times 100$$

The old standard solution should give detector responses of 10% or less of those of the new standard solution in order for the given standard solution to be considered stable under the storage conditions.

4.0 METHOD PROCEDURES

4.1 General Notes

4.1.1 The "◆" symbol indicates an optional stopping point after completing the indicated step. Samples may be stored overnight in a refrigerator (at or below 10°C).

4.1.2 The "~" symbol indicates approximately.

4.2 Soil Analysis

(Analysis of CGA 184927 and CGA 193469)

- ◆ 4.2.1 Weigh 20 g of a prepared* subsample of soil into a 250 mL polypropylene centrifuge bottle. Untreated control samples may be fortified at this point for determination of recovery. 100-200 μ L of the appropriate fortification standard (see 3.1.2) are added to the soil, mixed and let equilibrate for about 15 min.

* Subsample may be prepared by mixing with dry ice using a Hobart food chopper. These samples must be free-flowing and homogenous prior to subsampling.

4.2.2 Add 100 mL of 20:79:1 Water/acetone/acetic acid solution to the soil, shake using a platform shaker for ~30 min.

- ◆ 4.2.3 Remove and place in a sonic bath for ~10 minutes.

4.2.4 Centrifuge the sample at ~5000 RPM for at least 5 minutes or until separated and decant into a 500 mL separatory funnel.

4.2.5 Add 100 mL of 0.1N KOH and shake for 30 minutes at about 30°C.

4.2.6 Sonicate and adjust the pH to 3 ± 0.5 (using a pH meter) using 6N H_2SO_4 .

4.2.7 Centrifuge and combine with previous extraction solution into the 500 mL sep. funnel.

4.2 Soil Analysis cont'd

- 4.2.8 Add 300 mL of water to the sep. funnel.
- 4.2.9 Partition 2 times with 100 mL of dichloromethane (DCM) and dry through acid washed Na_2SO_4 .
- 4.2.10 Concentrate to a low final volume and use diazomethane to transfer to a 3.5 mL vial. Let stand for ~5 minutes, making sure the yellow color remains. Procedural standards of methylated CGA 193469 are prepared at this time as well.
- 4.2.11 Using a nitrogen evaporator adjust final volume to 2.0 mL in DCM. This final volume can range from 1.0 to 5.0 mL, depending on the sensitivity of the GC/MS.
- 4.2.12 Analysis is done by GC/MS using selective ion monitoring (see Section 5.0). These extracts can be stored at -20°C until analyzed by GC/MS.

5.0 INSTRUMENTATION GC/MS

(Equivalent instrumentation can be used)

5.1 GC/MS Conditions:

Instruments used:

HP 5890 Gas Chromatograph coupled with a HP 5971 Series Mass Selective Detector

HP 7673A Automatic Sampler

HP LaserJet Series II Printer

G1030A MS Chemstation (DOS Series)

Conditions:

Column - DB1701, J & W, 30m \times 0.25mm, 0.25 μm

Temp. Program: 100°C 0 min. to 280°C @ $10^\circ/\text{min}$, hold @ 280°C for 7 min.

Injector Temp. - 250°C , splitless injection mode

Detector Temp. (Interface) - 280°C

Carrier Gas - Helium

Flow rate - 60 mL/min.

Sample Inj. Volume - 2 μL

5.1 GC/MS Conditions: cont'd

Approximate Retention Times and Masses		
	m/z*	R.T. (min.)
CGA 184927	349,266,238	18.80
CGA 193469	325,266,238	17.27

Retention times may vary from those present above.

* Different ions may be selected if matrix interferences are present.

At the beginning of each GC/MS sequence, condition the inlet system by making 4-6 control soil extract injections.

Example chromatograms are attached (Appendix 1). Note that the retention times may vary from system to system and may require optimization.

5.2 Performance Criteria**First Criterion:**

Run a calibration standard on GC/MS at the LOQ of 0.030 ppm for CGA 193469 and at 0.10 ppm for CGA 184927 to meet sensitivity requirements ($S/N > 3:1$).

If this criteria cannot be met, optimize instrument operating parameters or change instrument method parameters such as multiplier voltage, replace the column guide or pre-column and clean the inlet.

Second Criterion:

Run a set of standards of four or more concentration levels, from 0.03 ppm to the highest concentration level to be included in the analysis. Generate a calibration curve for each analyte and obtain a linear regression with a correlation coefficient of at least 0.98 for each analyte. If this criterion is met, the samples may be run with standards interspersed with at least one standard at the beginning and one at the end of each sequence.

6.0 CALCULATIONS

6.1 Response Factor (R.F.):

$$R.F. = \frac{\text{Concentration of Standard (ppm)}}{\text{Peak Area of Standard}}$$

6.2 Concentration of Analyte in Soil (ppm):

$$\text{Conc. (ppm)} = \frac{(\text{Peak Area} \times R.F.) \times F.V.}{g.Extracted}$$

Where: Conc.(ppm) = Concentration of analyte in $\mu\text{g/g}$ (ppm)
F.V. = Final sample volume (mL)
g.Extracted = initial grams of sample extracted

6.3 % Recovery:

$$\% \text{ Recovery} = \frac{\text{Recovery Level (ppm)}}{\text{Fortification Level (ppm)}} \times 100$$

Recovery Level = Residue in the spiked control

7.0 SAFETY

Appropriate MSDS's should be available to the study personnel during the conduct of the study. General laboratory safety precautions should be taken. This method does not present any specific risks.

8.0 DETECTION LIMITS:

The LOQ for CGA 184927 and CGA 193469 is 0.030 ppm and 0.010 ppm respectively. The LOD was 0.010 ppm and 0.0030 ppm respectively based on a S/N of >3:1 of analyte to control soil background.

9.0 DISCUSSION:

Acceptable recoveries ranging from 71 to 130% and 65 to 120% for CGA 184927 and CGA 193469 respectively, were obtained at all fortification levels (ranging from 0.037 - 0.38 ppm for CGA 184927 and from 0.01 - 0.25 ppm for CGA 193469).

The overall average recovery for CGA 184927 was 102% with an RSD of 24% and for CGA 193469 was 87% with an RSD of 20%.

The RSD was higher than 20% for CGA 184927 since there was matrix effect on this ester which enhanced the response and gave some high recoveries.

There were no interferences observed in control samples.

10.0 TABLES:

TABLE 1: RECOVERY DATA* FOR CGA-184927 IN SOIL

LAB SAMPLE #	ANALYTE	AMOUNT SPIKED ($\mu\text{g/g}$)	AMOUNT FOUND ($\mu\text{g/g}$)	% RECOVERY
92-P1576-SPK 12	CGA-184927	0.037	0.048	130%
92-P1576-SPK 13	CGA-184927	0.037	0.047	127%
92-P1576-SPK 14	CGA-184927	0.037	0.041	111%
Average % Recovery - 123% SD - 10%				
92-P1576-SPK 1	CGA-184927	0.038	0.033	87%
92-P1576-SPK 3	CGA-184927	0.038	0.047	124%
92-P1576-SPK 5	CGA-184927	0.038	0.044	116%
92-P1576-SPK 7	CGA-184927	0.038	0.048	126%
92-P1576-SPK 9	CGA-184927	0.038	0.029	76%
92-P1576-SPK 11	CGA-184927	0.038	0.029	76%
Average % Recovery - 101% SD - 24%				
92-P1576-SPK 2	CGA-184927	0.38	0.48	126%
92-P1576-SPK 4	CGA-184927	0.38	0.31	82%
92-P1576-SPK 6	CGA-184927	0.38	0.27	71%
92-P1576-SPK 8	CGA-184927	0.38	0.27	71%
92-P1576-SPK 10	CGA-184927	0.38	0.39	103%
Average % Recovery - 91% SD - 24%				
Overall Average % Recovery - 102% SD - ± 24 RSD - 24%				

* These data were pooled from a soil dissipation study analyzed over a period of time. The response factors of the calibration standards varied from day to day thus peak areas are not presented.

10.0 TABLES:

TABLE 2: RECOVERY DATA* FOR CGA-193469 IN SOIL

LAB SAMPLE #	ANALYTE	AMOUNT SPIKED ($\mu\text{g/g}$)	AMOUNT FOUND ($\mu\text{g/g}$)	% RECOVERY
92-P1576-SPK 12	CGA-193469	0.010	0.0074	74%
92-P1576-SPK 13	CGA-193469	0.010	0.0071	71%
92-P1576-SPK 14	CGA-193469	0.010	0.0065	65%
Average % Recovery - 70% SD - 4.6%				
92-P1576-SPK 1	CGA-193469	0.025	0.19	76%
92-P1576-SPK 3	CGA-193469	0.025	0.021	84%
92-P1576-SPK 5	CGA-193469	0.025	0.035	140%*
92-P1576-SPK 7	CGA-193469	0.025	0.024	96%
92-P1576-SPK 9	CGA-193469	0.025	0.019	76%
92-P1576-SPK 11	CGA-193469	0.025	0.031	124%
* Outlier, not used in statistics.				
Average % Recovery - 91% SD - 20%				
92-P1576-SPK 2	CGA-193469	0.25	0.23	92%
92-P1576-SPK 4	CGA-193469	0.25	0.30	120%
92-P1576-SPK 6	CGA-193469	0.25	0.19	76%
92-P1576-SPK 8	CGA-193469	0.25	0.21	84%
92-P1576-SPK 10	CGA-193469	0.25	0.22	88%
Average % Recovery - 92% SD - 17%				

Overall Average % Recovery - 87%
SD - ± 17.9
RSD - 20%

* These data were pooled from a soil dissipation study analyzed over a period of time. The response factors of the calibration standards varied from day to day thus peak areas are not presented.

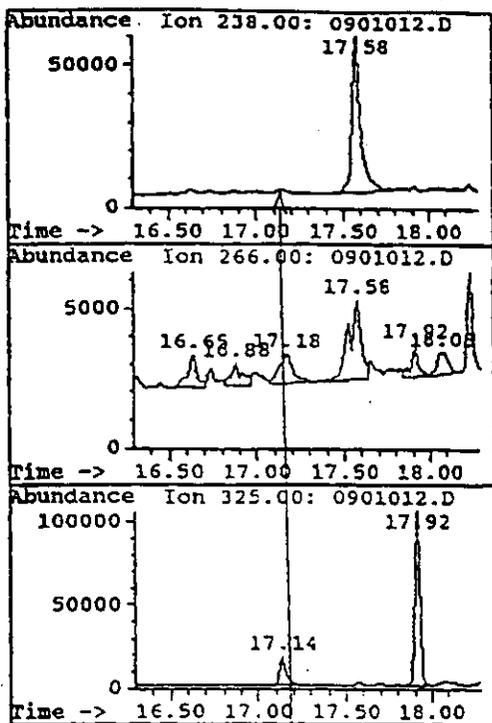
10.0 TABLES:

TABLE 3: SOIL CHARACTERIZATION SUMMARY

ETL SAMPLE #	FIELD PROJECT #	% SAND	% SILT	% CLAY	% ORGANIC MATTER
92-1576	3059/90	27	36	37	9.2

ETL SAMPLE #	FIELD PROJECT #	pH	CATION EXCHANGE CAPACITY CEC meq/100g	SOIL TYPE
92-1576	3059/90	6.3	32.5	clay loam black

**APPENDIX 1:
EXAMPLES OF CHROMATOGRAPHY**



File: C:\CHEMPC\DATA\CK03\0901012.D
 Operator: CK
 Data Acquired: 3 Feb 93 1:04 pm
 Method File: CGAMIX.M
 Sample Name: 92-P1576-26-1
 Misc Info:
 Vial Number : 9

CGA 193469

Ion 238.00: 0901012.D
92-P1576-26-1

Ret Time	Width	Area
17.577	0.088	1846928

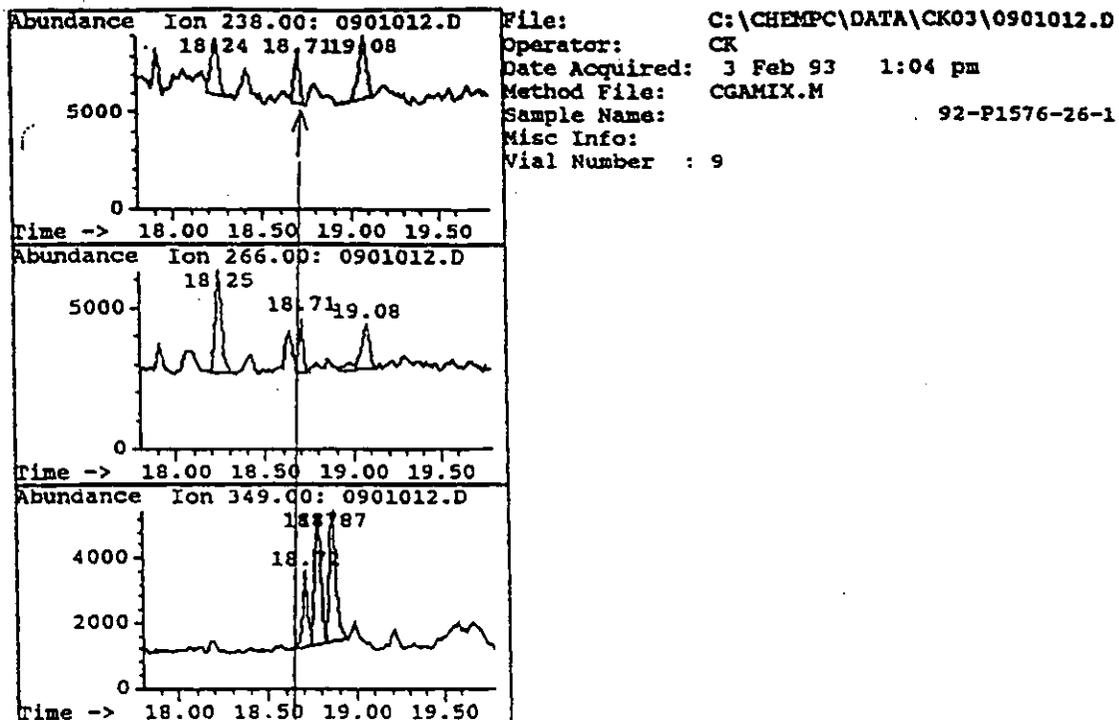
Ion 266.00: 0901012.D
92-P1576-26-1

Ret Time	Width	Area
16.645	0.055	40936
16.883	0.065	33184
17.176	0.073	58047
17.578	0.071	138899
17.918	0.052	32431
18.078	0.080	38816

Ion 325.00: 0901012.D
92-P1576-26-1

Ret Time	Width	Area
17.142	0.074	421267
17.922	0.050	2026772

Control Soil
(CGA 193469)



CGA 184927

Ion 238.00: 0901012.D
92-P1576-26-1

Ret Time	Width	Area
18.244	0.052	92748
18.710	0.038	64817
19.081	0.048	97397

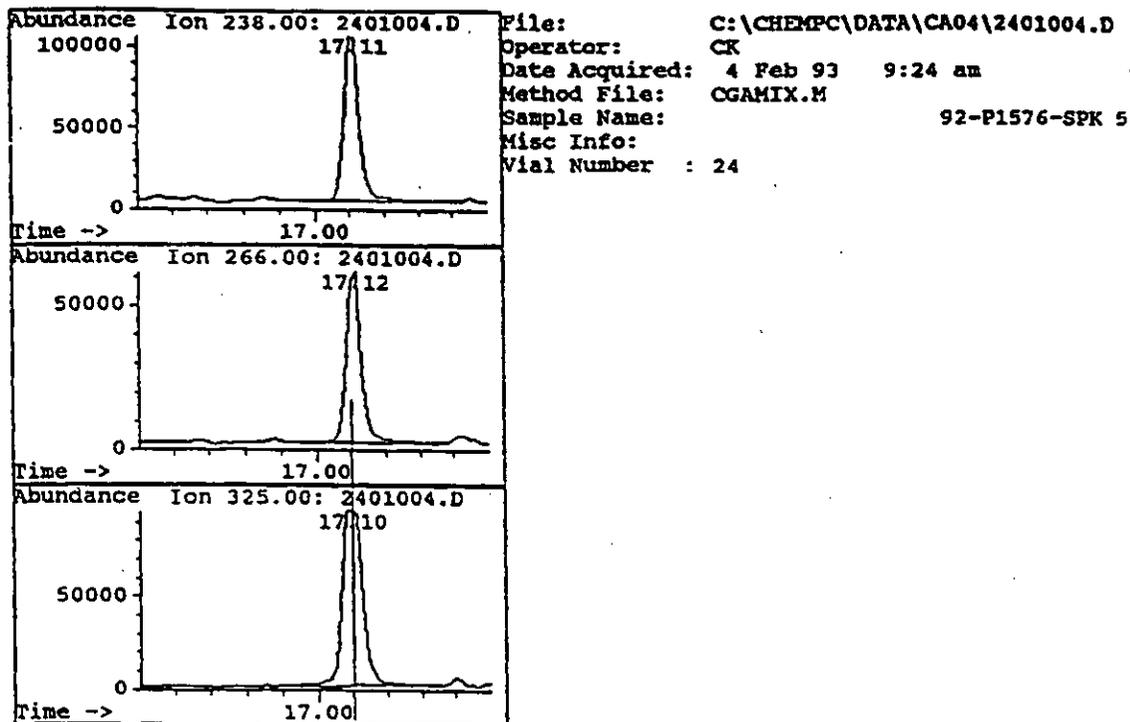
Ion 266.00: 0901012.D
92-P1576-26-1

Ret Time	Width	Area
18.247	0.044	91934
18.715	0.036	37167
19.079	0.059	60997

Ion 349.00: 0901012.D
92-P1576-26-1

Ret Time	Width	Area
18.718	0.038	45957
18.789	0.039	92917
18.869	0.045	103145

Control Soil <0.01 ppm
(CGA 184927)



CGA 193469

Ion 238.00: 2401004.D
 92-P1576-SPK 5-1

Ret Time	Width	Area
17.114	0.050	3120720

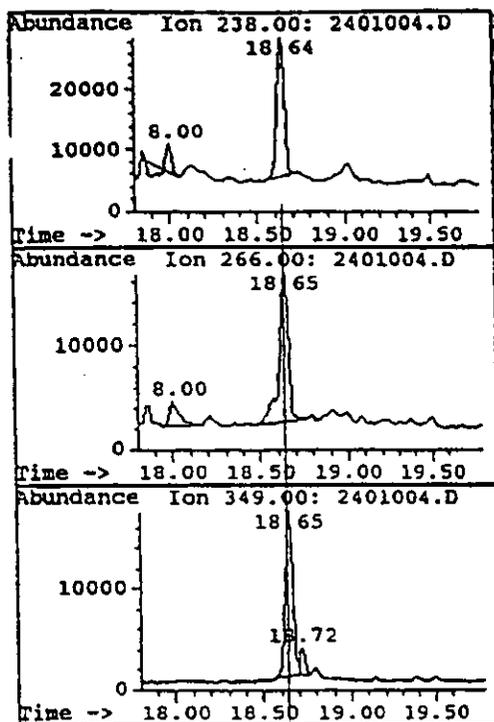
Ion 266.00: 2401004.D
 92-P1576-SPK 5-1

Ret Time	Width	Area
17.116	0.080	1779617

Ion 325.00: 2401004.D
 92-P1576-SPK 5-1

Ret Time	Width	Area
17.103	0.065	3947264

Control Soil spiked at 0.025 ppm
 (CGA 193469)



File: C:\CHEMPC\DATA\CA04\2401004.D
Operator: CK
Date Acquired: 4 Feb 93 9:24 am
Method File: CGAMIX.M
Sample Name: 92-P1576-SPK 5
Misc Info:
Vial Number : 24

CGA 184927

Ion 238.00: 2401004.D
92-P1576-SPK 5-1

Ret Time	Width	Area
18.003	0.013	37012
18.645	0.047	670585

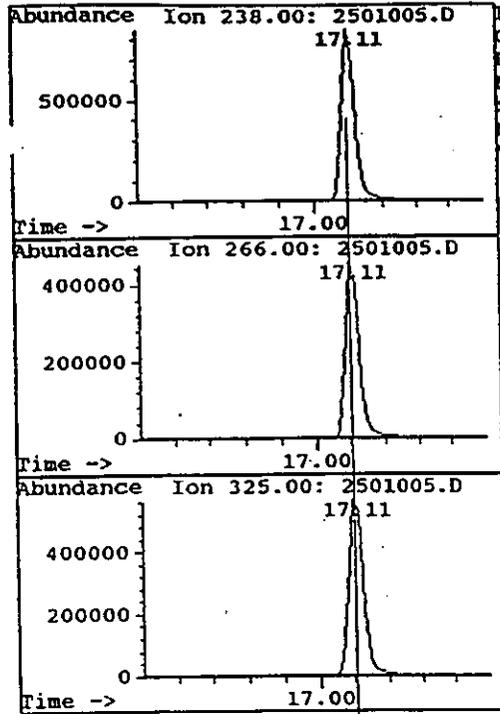
Ion 266.00: 2401004.D
92-P1576-SPK 5-1

Ret Time	Width	Area
18.003	0.070	98909
18.646	0.053	510128

Ion 349.00: 2401004.D
92-P1576-SPK 5-1

Ret Time	Width	Area
18.652	0.044	427393
18.723	0.039	60675

Control Soil spiked at 0.038 ppm
(CGA 184927)



File: C:\CHEMPC\DATA\CA04\2501005.D
 Operator: CK
 Date Acquired: 4 Feb-93 9:51 am
 Method File: CGAMIX.M
 Sample Name: 92-P1576-SPK 6
 Misc Info:
 Vial Number : 25

CGA 193469

Ion 238.00: 2501005.D
 92-P1576-SPK 6-1

Ret Time	Width	Area
17.110	0.042	21881491 X

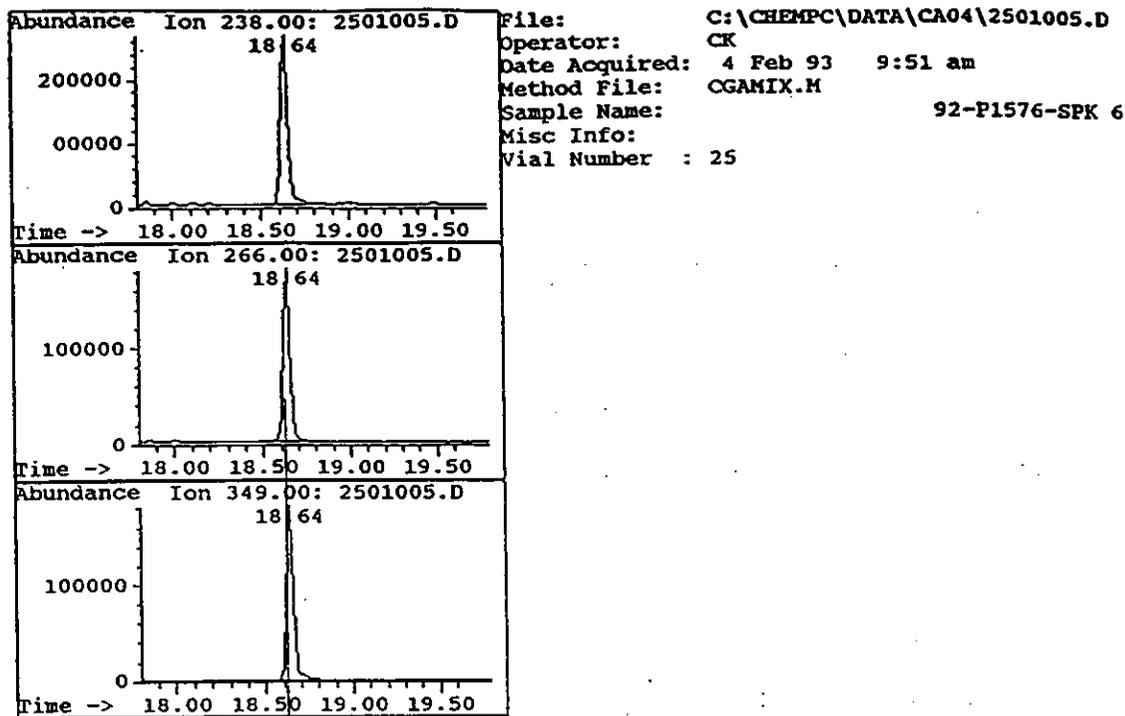
Ion 266.00: 2501005.D
 92-P1576-SPK 6-1

Ret Time	Width	Area
17.112	0.042	12069666

Ion 325.00: 2501005.D
 92-P1576-SPK 6-1

Ret Time	Width	Area
17.113	0.045	16338937

Control Soil spiked at 0.25 ppm
 (CGA 193469)



CGA 184927

Ion 238.00: 2501005.D
92-P1576-SPK 6-1

Ret Time	Width	Area
18.636	0.047	7388089

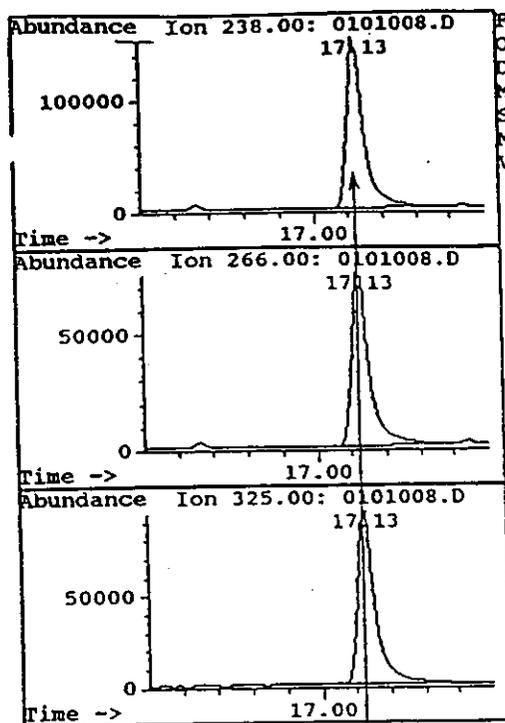
Ion 266.00: 2501005.D
92-P1576-SPK 6-1

Ret Time	Width	Area
18.638	0.068	4681614

Ion 349.00: 2501005.D
92-P1576-SPK 6-1

Ret Time	Width	Area
-18.642	0.044	4716373

Control Soil spiked at 0.38 ppm
(CGA 184927)



File: C:\CHEMPC\DATA\CA04\0101008.D
Operator: CK
Date Acquired: 4 Feb 93 11:14 am
Method File: CGAMIX.M
Sample Name: 1 PPM CGA MIX
Misc Info:
Vial Number : 1

CGA 193469

Ion 238.00: 0101008.D
1 PPM CGA MIX

Ret Time	Width	Area
17.127	0.056	5048843

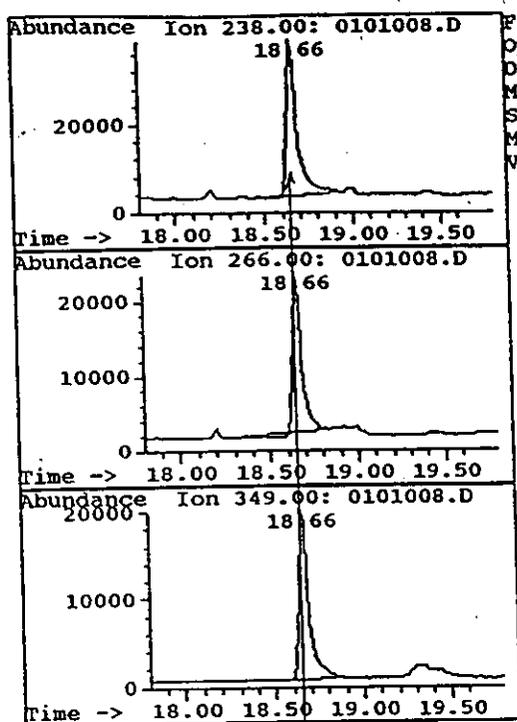
Ion 266.00: 0101008.D
1 PPM CGA MIX

Ret Time	Width	Area
17.130	0.052	2604388

Ion 325.00: 0101008.D
1 PPM CGA MIX

Ret Time	Width	Area
17.132	0.052	3250844

Standard at about 1 ppm
(CGA193469)



File: C:\CHEMPC\DATA\CA04\0101008.D
 Operator: CK
 Date Acquired: 4 Feb 93 11:14 am
 Method File: CGAMIX.M
 Sample Name: 1 PPM CGA MIX
 Misc Info:
 Vial Number : 1

CGA 184927

Ion 238.00: 0101008.D
1 PPM CGA MIX

Ret Time	Width	Area
18.658	0.062	1460072

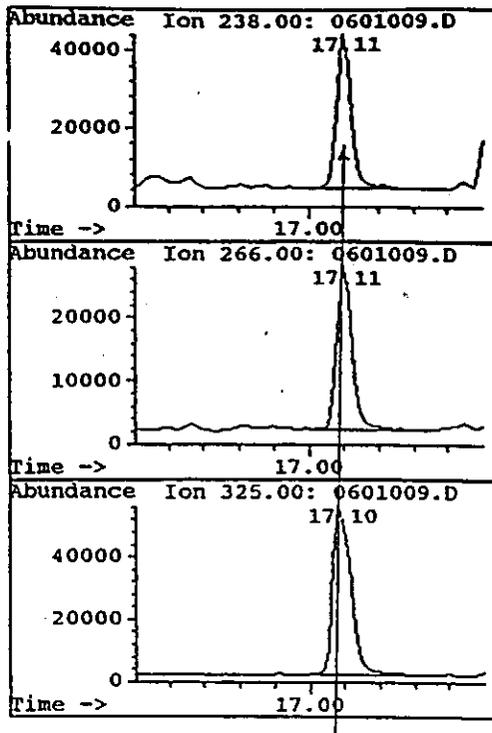
Ion 266.00: 0101008.D
1 PPM CGA MIX

Ret Time	Width	Area
18.658	0.052	710435

Ion 349.00: 0101008.D
1 PPM CGA MIX

Ret Time	Width	Area
18.661	0.058	772297

Standard at about 1 ppm
(CGA184927)



File: C:\CHEMPC\DATA\CA04\0601009.D
Operator: CK
Date Acquired: 4 Feb 93 11:41 am
Method File: CGAMIX.M
Sample Name: 92-P1576-43-1
Misc Info:
Vial Number : 6

CGA 193469

Ion 238.00: 0601009.D
92-P1576-43-1

Ret Time	Width	Area
17.110	0.045	1128758

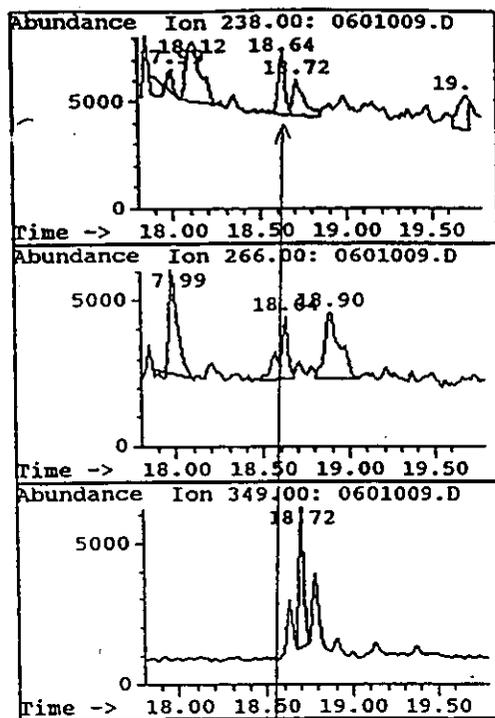
Ion 266.00: 0601009.D
92-P1576-43-1

Ret Time	Width	Area
17.110	0.049	771446

Ion 325.00: 0601009.D
92-P1576-43-1

Ret Time	Width	Area
17.096	0.062	1991812

Treated Soil sample with
0.015 ppm CGA193469



File: C:\CHEMPC\DATA\CA04\0601009.D
 Operator: CK
 Date Acquired: 4 Feb 93 11:41 am
 Method File: CGAMIX.M
 Sample Name: 92-P1576-43-1
 Misc Info:
 Vial Number : 6

**CGA 184927 Ion ratios
differ from standard**

Ion 238.00: 0601009.D
92-P1576-43-1

Ret Time	Width	Area
17.993	0.017	10084
18.120	0.089	164760
18.636	0.043	71444
18.723	0.063	72523
19.709	0.063	59935

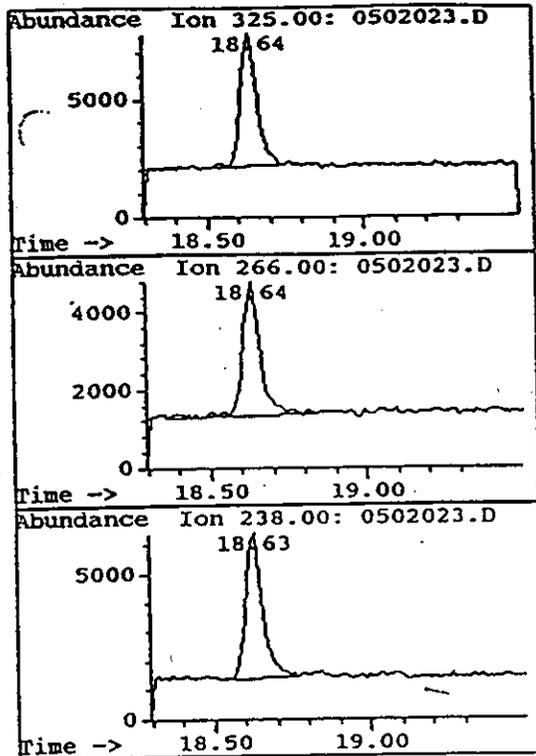
Ion 266.00: 0601009.D
92-P1576-43-1

Ret Time	Width	Area
17.988	0.050	115403
18.638	0.068	76187
18.897	0.102	137941

Ion 349.00: 0601009.D
92-P1576-43-1

Ret Time	Width	Area
18.717	0.046	91666

Treated Soil sample with
<0.01 ppm CGA184927



File: C:\CHEMPC\DATA\MH03\0502023.
Operator: CK
Date Acquired: 8 Mar 93 10:03 pm
Method File: CGMIX.M
Sample Name: 92-P1576-SPK
Misc Info: 92FSN02
Vial Number : 5

CGA 193469

Ion 325.00: 0502023.D
92-P1576-SPK 13-1

Ret Time	Width	Area
18.638	0.058	215243

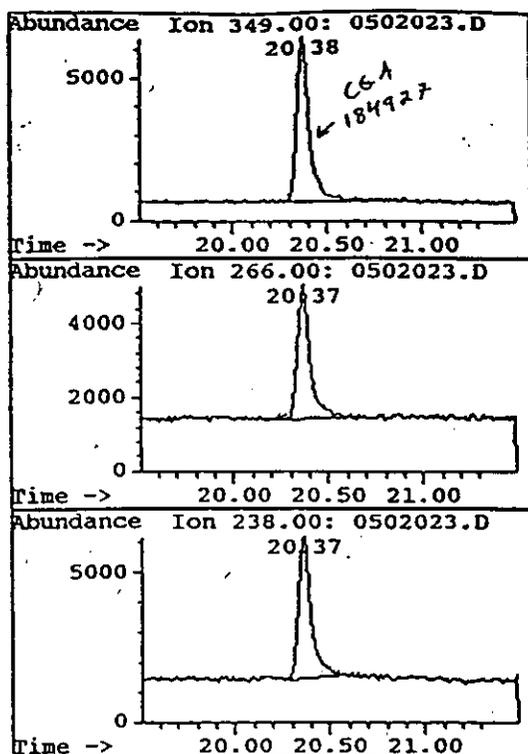
Ion 266.00: 0502023.D
92-P1576-SPK 13-1

Ret Time	Width	Area
18.635	0.064	137410

Ion 238.00: 0502023.D
92-P1576-SPK 13-1

Ret Time	Width	Area
18.631	0.058	190698

Soil spiked at LOQ (0.01 ppm)
(71%) (CGA 193469)



File: C:\CHEMPC\DATA\MH03\0502023.
 Operator: CK
 Date Acquired: 8 Mar 93 10:03 pm
 Method File: CGAMIX.M
 Sample Name: 92-P1576-SPK
 Misc Info: 92FSN02
 Vial Number : 5

CGA 184927

Ion 349.00: 0502023.D
 92-P1576-SPK 13-1

Ret Time	Width	Area
20.377	0.071	266507

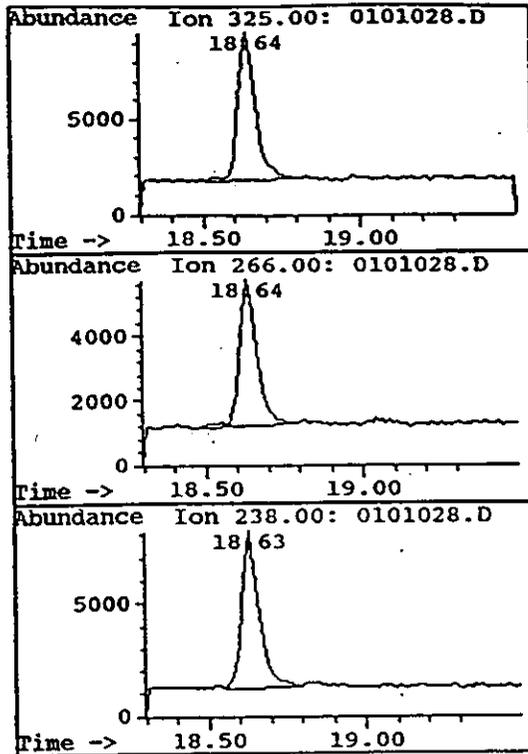
Ion 266.00: 0502023.D
 92-P1576-SPK 13-1

Ret Time	Width	Area
20.375	0.071	168956

Ion 238.00: 0502023.D
 92-P1576-SPK 13-1

Ret Time	Width	Area
20.371	0.070	225739

Soil spiked at LOQ (0.03 ppm)
 (127%) (CGA 184927)



File: C:\CHEMPC\DATA\MH03\0101028.
 Operator: CK
 Date Acquired: 4 Mar 93 0:20 am
 Method File: CGAMIX.M
 Sample Name: 0.2PPM CGA
 Misc Info: 92FSN02
 Vial Number : 1

CGA 193469

Ion 325.00: 0101028.D
0.2PPM CGA

Ret Time	Width	Area
18.642	0.061	310519

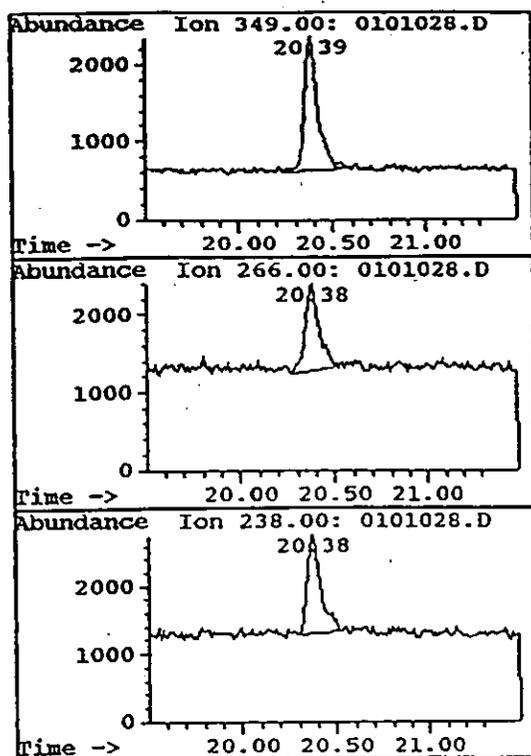
Ion 266.00: 0101028.D
0.2PPM CGA

Ret Time	Width	Area
18.637	0.060	182343

Ion 238.00: 0101028.D
0.2PPM CGA

Ret Time	Width	Area
18.635	0.059	264105

0.2 ppm Standard
(CGA 193469)



File: C:\CHEMPC\DATA\MH03\0101028.
 Operator: CK
 Date Acquired: 4 Mar 93 0:20 am
 Method File: CGAMIX.M
 Sample Name: 0.2PPM CGA
 Misc Info: 92FSN02
 Vial Number : 1

CGA 184927

Ion 349.00: 0101028.D
 0.2PPM CGA

Ret Time	Width	Area
20.386	0.076	87169

Ion 266.00: 0101028.D
 0.2PPM CGA

Ret Time	Width	Area
20.383	0.078	57739

Ion 238.00: 0101028.D
 0.2PPM CGA

Ret Time	Width	Area
20.379	0.075	72889

0.02 ppm Standard (CGA 184927)

**APPENDIX 2:
STANDARD OPERATING PROCEDURES**

EFFECTIVE: JULY23/92

REF: # PSOP3.01
page 1 of 4**STANDARD OPERATING PROCEDURE****PREPARATION OF DIAZOMETHANE**

1. Purpose: - Diazomethane is a reagent used to derivatize herbicide acids forming the more volatile methyl esters.

2. Principle: - A solution of Diazald (N-methyl-N-nitroso-p-toluene sulfonamide) is placed in a hot water bath. A solution of potassium hydroxide in water is added dropwise to the Diazald. The resulting product, diazomethane, is slowly distilled into a flask.

3. Safety: - Diazomethane is highly toxic, carcinogenic, and potentially explosive. All work must be done in a fume hood to avoid inhalation. Explosions have been observed when there is contact with alkali, metals, rough surfaces, or heat (100°C). Most diazomethane explosions occur during distillation so all glassware used must be free of sharp edges, etches, scratches, or ground-glass joints. Wash all glassware with care and the use of wire brushes must be avoided. Hood sash must be closed during distillation in case of explosion.

4. Apparatus and Reagents: - Diazald Kit parts list:

- 1) Claisen adapter
- 2) Connecting adapter
- 3) Vacuum distilling adapter
- 4) Distilling column, 200 mm
- 5) Round-bottom flask, 50 ml
- 6) Round-bottom flask, 100 ml
- 7) Separatory funnel with teflon stopcock, 125 ml
- 8) Teflon stopper

EFFECTIVE: JULY23/92

REF: # PSOP3.01
page 2 of 4

graduated cylinders, 50 ml, 25 ml
flask, erlenmeyer, 125 ml
flask, erlenmeyer, 125 ml, joint (narrow, no ground glass)
scoops, stainless steel
diethyl ether, Caledon, distilled in glass
water, de-ionized
N-methyl-N-nitroso-p-toluene sulfonamide
(Diazald), Aldrich
methanol, pesticide grade
beakers, pyrex (for hot and cold water baths)

5. Procedure: A) Set up the apparatus as shown in Figure 1.
- B) Weigh 10.0 g of Diazald into a 100 ml round-bottom flask and add 130 ml of diethyl ether. Swirl until dissolved.
- C) Weigh 3.3 g of KOH into a 125 ml erlenmeyer flask and dissolve in 75 ml of methanol. Add 45 ml of this solution to the separatory funnel and discard the rest (or label and store in a freezer).
- D) Place a bath of hot (tap) water under the flask and ice water under the receiving flask. Use ice water only if the humidity is low.
- E) Check to see if all joint connections are tight and there is cold water flowing through the distilling column before proceeding.
- F) Open the stopcock on the separatory funnel allowing the KOH solution to drip slowly (about 1 drop/second) into the Diazald/ether mix. (Note: Immediately after the KOH solution has been added, close the stopcock to prevent any product losses).

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PSOP3.01
page 3 of 4

G) The bright yellow product will begin to distill into the receiving flask. (The hot water bath may be replaced when necessary to speed up the reaction). When the distilling ether turns colorless, the reaction is complete.

H) Pour the final product into 50mL test tubes (that have been blown out with nitrogen) with teflon lined caps and store in WIC #2 in a dessicator. Label with preparation date, expiry date, your initials, and "distilled" on the tubes. Expiry date is 2 weeks from date of preparation.

I) After cooling the reaction flask, disassemble, and discard the ether mixture in a waste solvent receptacle. Carefully wash all parts of the distillation apparatus and store in the kit provided.

NOTE: IT HAS BEEN OBSERVED THAT THERE IS A PROBLEM WITH THE DIAZOMETHANE WHEN THE HUMIDITY IS HIGH. BECAUSE OF THIS, THE TEST TUBES SHOULD BE STORED IN A DESSICATOR WITH DRIERITE. ALSO THE RECEIVING FLASK SHOULD BE COOLED WITH ICE WATER ONLY WHEN THE HUMIDITY IS LOW SO THAT WATER DOES NOT CONDENSE ON THE INSIDE OF THE FLASK.

Preparer:



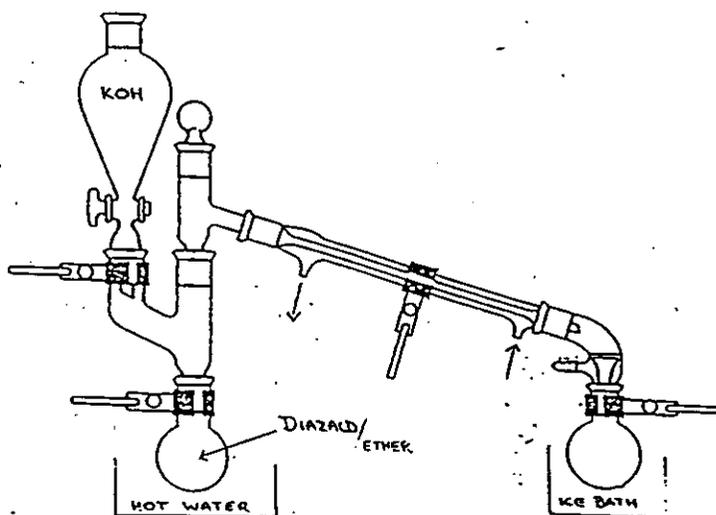
Management:



EFFECTIVE: JULY23/92

REF: # PSOP3.01
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Figure 1
Set-up of Diazald Kit for diazomethane generation



ETL

EFFECTIVE DATE: July 17, 1995
REVIEW DATE: 2 YEARSREF#:GSOP10.02
PAGE 1 OF 2STANDARD OPERATING PROCEDURE
REGULAR BAKED AND ACIDIFIED Na_2SO_4

1. Purpose: When performing solvent extractions, the solvent layer is dried by passing it through a layer of Na_2SO_4 . Regular baked and acidified Na_2SO_4 are used in base-neutral and acid extraction procedures (respectively).
2. Safety: When handling concentrated H_2SO_4 , special care must be taken as this acid is highly corrosive and causes severe burns. Gloves, safety glasses and protective clothing must be worn and all work must be done in a fume hood.
3. Apparatus: crucible, 250 mL
1000 mL round- bottom flask
filtering flask, 2 - litre
Büchner funnel, large (15 cm)
filtervac, rubber
filter paper, Whatman No. 4, 15.0 cm
stirring rod, glass, large
graduated cylinder, 10 mL
aluminum pan
glass jars, 2 - litre, with Teflon lined caps
 Na_2SO_4 , ACS grade, granular, anhydrous
 H_2SO_4 , Fisher, ACS grade
ethyl ether, BDH, distilled in glass
4. Procedure: A) Regular Baked Na_2SO_4
 1. Fill a crucible with Na_2SO_4 and bake at 500°C for at least 4 hours in a muffle oven.
 2. Take out of oven and cover until cool.
 3. Once cooled, store in a glass jar.

B) Acidified Na_2SO_4

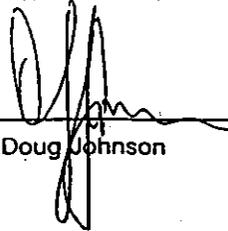
 1. Fill a 1000 mL round bottom 2/3 full with regular baked Na_2SO_4 .
 2. Add ethyl ether until the surface of the Na_2SO_4 is covered.

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EFFECTIVE DATE: July 17, 1995
REVIEW DATE: 2 YEARSREF#:GSOP10.02
PAGE 2 OF 2B) Acidified Na₂SO₄ ... continued

3. Using a Pasteur pipet, slowly add 1-2 mL of concentrated H₂SO₄ to the round bottom.
4. Stopper the round bottom with ground glass stopper and invert several times to mix.
5. Set up filtering apparatus and connect to an aspirator (not vacuum line) in fume hood.
6. Pour acidified Na₂SO₄/ether mixture into Büchner funnel and allow the ether to filter off for 5 minutes.
7. Transfer the acidified Na₂SO₄ to an aluminum pan and allow to air-dry in the fume hood until free flowing (~2 hours).
8. Once dried, transfer to a glass jar and label ("Acidified Na₂SO₄", analyst's initials, date of preparation).

Prepared: 
Heather GordonDate: 07/18/95Approved: 
Doug JohnsonDate: 07/18/95

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