Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: MCPA

MRID #: 421340-01

Matrix: Soil

Analysis: GC/ECD

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DATE: 06/05/90
REPLACES: 03/18/90
SECTION: 6001

ANALYTE: Determination of MCPA in Soil

AREA OF APPLICABILITY: Hazleton Laboratories America, Inc. (HLA)
Regulatory Compliance Monitoring

SCOPE:

This method is applicable to soil levels in the range from 0.05 µg/g [limit of detection (LOD)] to 1,000 µg/g (higher if dilutions are made).

PRINCIPLE:

Soil samples are homoginized, blender extracted with 35:65 water:acetonitrile, filtered, and oxidized with potassium hydroxide. The extract is partially cleaned by a partition with chloroform after adding sodium chloride and sodium hydroxide. The chloroform is discarded. The sample is then acidified with sulfuric acid and partitioned with chloroform. The sample is reduced in volume and derivatized with diazomethane. Following derivatization, the samples are further cleaned by Florisil and then injected and quantitated using a gas chromatograph (GC) with a Hall detector.

SENSITIVITY:

The lowest detection limit of this assay is 0.05 µg/g. The highest limit is 1,000 µg/g for each compound.

PRECISION AND ACCURACY:

Recovery data for Project No. 6237-118C (MCPA isooctyl ester) show that the range of recoveries are 98% to 122% (on a ppm basis), with a mean of 106% and a standard deviation of 8.73%.

For Project No. 6237-118D (MCPA isooctyl ester), the range was from 76% to 119% (on a ppm basis), with a mean of 103% and a standard deviation of 13.68%.

Note: Each set of recoveries was run in duplicate at three spiking levels:

70 µL of 60.4 µg/mL MCPA isooctyl ester
35 µL of 604 µg/mL MCPA isooctyl ester
125 µL of 604 µg/mL MCPA isooctyl ester

REFERENCES:

Khan, Shahamat U., "Electron Capture Gas-Liquid Chromatographic Method for the Simultaneous Analysis of 2,4-D, Dicamba, and Mecoprop Residues in Soil, Wheat, and Barley," JAOAC, 58(5) (1975).

Garbrecht, Thomas P., Sr., "Rapid Esterification of Dicamba and Chlorophenoxy Acids with N<O-bis (Trimethylsilyl) Acetamide for Gas Chromatographic Analysis," JAOAC, 53(1) (1970).

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(1398D)

SAFETY PRECAUTIONS:

- Observe all laboratory safety precautions as outlined by the HLA Safety Training Manual.
- Take care when working with organic solvents; the fumes may be harmful.

INTERFERENCES:

No known interferences exist.

QUALITY ASSURANCE:

- A recovery and control sample are run with each set of samples (a set is no larger then 20 samples). The recovery is spiked at one to five times the LOD.
- A reagent blank and reagent spike sample may be run with each set of samples; this is optional.

APPARATUS:

- Analytical balance, precise to 0.02 g
- Rotary evaporation equipment
- Steam bath
- Blender motor
- Blender cups, 40-oz capacity
- Buchner funnels
- Vacuum flasks
- Kuderna-Danish (K-D) flasks, 500-mL capacity
- K-D tubes, 25- to 50-mL capacity
- 3-ball Snyder columns
- 250-mL separatory flasks
- 250- to 500-mL boiling flasks
- Powder funnels
- Cotton batting
- 15- to 20-mm watch glass
- Chromatographic columns, 19-mm i.d. x 30 cm (approximate), with a 200- to 300-mL reservoir and fritted end
- GC injection vials
- Gas chromatograph with Hall Detector in halogen mode
- Various normal glassware
- 10-mL volumetric flasks

REGENTS:

- Florisil, 100-200 mesh, residue grade, activated
- Acetonitrile, residue grade
- Deionized water
- Extraction solvent, 65% acetonitrile/35% water (v/v)
- Acid-washed celite
- 0.5N methanolic potassium hydroxide (28.1 g potassium hydroxide in 1-L methanol)
- Boiling chips
- Sodium chloride
- 3N sodium hydroxide
- Chloroform, residue grade
- Petroleum ether, residue grade
- Anhydrous sodium sulfate
- Elution solvent, 19% ethyl ether, 1% ethanol, 80% petroleum ether (v/v/v)
- Water, purified through a Milli-Q® system, Millipore Corporation
- 6N sulfuric acid
- Isooctane, residue grade
- Diazomethane. Combine 35 mL of 2-(2-ethoxyethoxy)ethanol, 20 mL of ether, and a potassium hydroxide solution (6 g of potassium hydroxide in 10 mL of water). Place this solution in a 100-mL long-necked distilling flask fitted with a dropping funnel and an efficient condenser, in a water bath at 40°C. As the distillation of the ether starts, add a solution of 21.4 g of Diazald® (an Aldrich product, D2,800-0) in about 200 mL of ether through the dropping funnel over 20 minutes. The rate of addition should equal the rate of distillation. When the dropping funnel is empty, add another 40 mL of ether slowly and continue the distillation until the distilling ether is colorless. The combined ethereal distillates contain about 3 g of diazomethane.

CAUTION: Diazomethane is not only exceedingly toxic, but its solutions have been known to explode unaccountably. Hence, all work with diazomethane should be carried out behind safety shields in efficient hoods, and proper respirator masks should be worn.

NOTE: Diazomethane should be made by an experienced analyst.

PROCEDURE:

Extraction, Partition, and Derivatization

NOTE: A recovery sample should be fortified immediately after transfer to a Waring blender with the appropriate volume of spiking standards.

1. Transfer 50.0 g of the sample into a Waring blender.

2. Add 350 mL of extraction solvent (35% Milli-Q water:65% acetonitrile) and blend it at moderate speed for 3 minutes.

3. Filter the solution through a Buchner funnel lined were with a Whatman No. 5 filter paper and approximately 3/4 in. of acid-washed celite. Do not rinse the celite.

4. Transfer 100 mL of filtrate to a K-D apparatus containing 25 mL of 0.5N alcoholic potassium hydroxide and a large boiling chip. Save the remaining filtrate in an 8-oz jar with an aluminum foil-lined cap.

5. Attached a three-ball Snyder column to the K-D apparatus and support it on a steam bath with a bottomless beaker. Keep the steam low until all places on the steam bath are filled, then increase the heat and evaporate the samples to an aqueous layer. The aqueous layer is reached when there is no longer action from the top ball on the Snyder column. Remove the layer from the heat and allow it to cool.

6. Rinse the Snyder column with a few milliliters of Milli-Q water and remove the column.

7. To a 250-mL separatory funnel containing approximately 5 g of sodium chloride, add the aqueous layer from the K-D apparatus with small Milli-Q rinses. Rinse the K-D apparatus with 10 mL of 3N sodium hydroxide and add it to the separatory funnel. Shake the separatory funnel to dissolve the sodium chloride. Rinse the K-D apparatus with approximately 25 mL of chloroform and add it to the separatory funnel.

8. Gently invert the separatory funnel six to eight times, venting it as necessary. Allow the layers to separate, then discard the lower chloroform layer. Do not discard any emulsion that might appear between layers.

9. Repeat Step 8 with another 25 mL of chloroform and discard the lower layer as before.

10. Add 15 mL of 6N sulfuric acid and mix it slightly.

11. Add 25 mL of chloroform, stopper the separatory funnel, and shake it for 1 minute.

12. Allow the layers to separate and pass the lower chloroform layer through a plug of glass wool, supported by a glass funnel placed in a 250-mL round-bottom flask.

13. Repeat Steps 11 and 12 twice more.

14. Rinse the cotton with a small amount of chloroform, remove the funnel, and add 5 mL of isooctane to each flask.

15. Evaporate the extract to approximately 2 mL.

16. Under an exhaust hood, add 5 mL of diazomethane to each flask, cover the flasks with watch glasses, and allow them to stand for 30 minutes.

17. Add 5 mL of isooctane and evaporate the solution to approximately 2 mL.

18. Add 5 mL of petroleum ether to each flask and cover the flasks with aluminum foil.

NOTE: Blender jars, Buchner funnels, and K-D apparati should be cleaned by the analyst immediately after use.

Florisil Cleanup

1. Add 35 mL of profiled Florisil to the column and tap the column to settle it. Top the florisil with approximately 1.5 cm of anhydrous sodium sulfate.

2. Prewash the column with 70 mL of petroleum ether.

3. When the petroleum ether has just entered the sodium sulfate layer, add the sample to the column. Rinse the round-bottom flask with two 5-mL portions of petroleum ether and add them to the column.

4. Place a clean 250- or 500-mL boiling flask under the column and elute the sample with 200 mL of the elution solvent.

5. Add 5 mL of isooctane to the boiling flask and evaporate the sample to just under 5 mL.

6. Quantitatively transfer the sample to a 10-mL volumetric flask and dilute it to volume.

7. Transfer the sample to a screw-top injection vial and retain excess sample in 2-dram vail.

8. Inject the sample into the GC system and quantitate it.

GC Conditions

Column:	3% OV-17 on 100/120 mesh supelcoport 4 mm i.d.-x 6 ft.
Injection port:	250°C
Detector:	Halogen mode, 900° to 1,000°C
Column temperatures:	Initial, 175°C
	Final, 190°C
	Rate, 3°C/minute
Injector volume:	7 µL
Carrier gas:	Helium, 40 mL/minute
Reaction gas:	Hydrogen, 50 mL/minute

NOTE: The above parameters may be adjusted to maximize chromatographic resolution and instrument performance.

CALCULATIONS:

Using standards of appropriate concentration, calibrate a standard curve of peak height of MCPA methylated acid versus concentration. Compare sample peak heights to the standard curve of concentration values. Sample peak heights should fall between the standard run for proper quantitation (limit approximately 0.05 µg/mL for standard).

$$ppm = \frac{G \times D}{S} \times 1.56$$

where ppm = concentration of MCPA ester in sample
G = µg/mL MCPA acid in sample generated from standard curve
D = dilution volume (mL)
S = sample weight (g)
1.56 = conversion factor MCPA acid to MCPA ester

(MCPE)