Determination of Methomyl Residues in Soil

M.L. Method No.: DUP-89AM-001

Procedure:

Method Reference:

Extraction and Clean Up

1. J. Agr. & Food Chem. 16(2):554.1968.
2. J. Agr. & Food Chem. 24(2):263.1976.
3. Oxamyl Cleanup Procedure for Onions, Cabbage and Brussel Sprouts, DuPont Undated Report.

HPLC Analysis

1. The State of California: Recommended Methods of Analysis for the Organic Components Required for AB1803, Method No. 632, May, 1985.

Sample Preparation:

Thoroughly mix frozen sample and weigh a representative amount for analysis.

Dry Weight Determination:

Weigh into a preweighed disposable metal pan a 10.00 g representative sample of soil. Dry the sample to a constant weight at 135 C and record the sample dry weight for use in calculations.

Extraction and Fortification:

1. Weigh a 25.0 g representative sample into a 500 mL erlenmeyer flask with ground glass stopper. For recovery study, fortify at this point and allow the solvent from the spiking standard to evaporate completely before proceeding with the next step.

2. Thoroughly wet the sample with deionized water. Add 100 mL HPLC grade ethyl acetate. Stopper the flask securely and shake in a wrist action shaker at high speed for 15 minutes.

3. Decant the ethyl acetate through #541 Whatman filter paper (or equivalent) into a 500 mL evaporating flask.

4. Repeat the extraction and filtration steps 2 more times, each time using 100 mL ethyl acetate only.

5. Evaporate the combined ethyl acetate extract at less than 40 C to 5 mL for silica gel column cleanup.

Silica Gel Column Cleanup:

1. Prepare silica gel, 7% activated with deionized water, the day before column cleanup step in order to allow the activated absorbent to equilibrate overnight in a tightly sealed container. (Silica gel: Davison Chemical Co., grade 923, mesh 100-200 and allowed to dry at 135 C for a minimum of 18 hours).

2. Transfer 20 grams of activated silica gel to a 2.5 cm x 300 mL chromatographic column. Top with 5 mL anhydrous sodium sulfate and prewash column with 50 mL HPLC grade hexane.

3. Transfer the sample extract (in 5 mL ethyl acetate) to the column.

4. Wash the sample flask with 2 x 5 mL hexane and allow the solvent from the column application to drain. Discard solvent collected from this step.

5. Wash the column with 200 mL 1:1 hexane:ethyl acetate and discard this wash.

6. Elute methomyl with 200 mL of 10% HPLC grade methanol in ethyl acetate into a 500 mL evaporating flask.

7. Evaporate the eluate at less than 40 C to about 2 mL and transfer to a test tube using about 2 mL ethyl acetate for rinsing and transfer.

8. Evaporate the extract to about 0.2 mL in a 40 C water bath and store in the freezer for HPLC analysis.

Standard:

The standard used was methomyl from Chem Serv., Lot No. 14-114, PS-775 and had a 99% purity.

Fortification:

The check samples were spiked in ethyl acetate and extracted like the samples.

HPLC Analysis:

1. Just prior to HPLC analysis, blow the sample extract to dryness with a gentle stream of nitrogen and dissolve the sample residue in 2.5 mL of mobile phase for HPLC analysis so that 1 mL of extract equals 10 g of sample.

2. Analyze the samples and standards for methomyl using the following conditions:

Instrument:	SP8450-2 with SP8770-2
Column:	4.6 mm x 25 cm DuPont Zorbax ODS, 5 u particle size
Mobile Phase:	84% water, 15% acetonitrile, 1% acetic acid
Column Temperature:	Ambient
Flow Rate:	0.8 mL/min
Detector:	UV at 233 nm

Calculations:

Suitable concentrations of standards containing methomyl were injected into the HPLC to construct a standard curve based on peak height (in mm) of standards. Peaks below 100 mm were measured to nearest 0.5 mm. Peaks above 100 mm were measured to nearest mm. The amount of methomyl residue in the sample was calculated using the following equation:

$$ppm = \frac{ng}{mg}, \quad \text{where}$$

ppm = parts per million methomyl in the sample.

ng = ng methomyl from the standard curve based on peak height response of extract.

mg = mg sample extract injected into the HPLC.

For Example:

1. For M.L. No. 50382, check:

0.0 mm peak height was equivalent to 0.0 ng methomyl from the standard curve.

$$ppm = \frac{0.0 \text{ ng methomyl}}{200 \text{ mg sample}} = 0.0 \text{ ppm}, \quad \text{which was less than 0.02 ppm}$$

2. For M.L. No. 50382, spike 3:
98.0 mm peak height was equivalent to 40.0 ng methomyl from the standard curve.

$$\text{ppm} = \frac{40.0 \text{ ng methomyl}}{200 \text{ mg sample}} = 0.200 \text{ ppm}$$

3. $$\% \text{ Recovery} = \frac{(\text{ppm methomyl in spike sample} - \text{ppm methomyl in check sample})^{*}}{\text{Fortification level (ppm)}} \times 100$$

For M.L. No. 50382, spike 3:

$$\% \text{ recovery} = \frac{0.200 \text{ ppm} - 0.0 \text{ ppm}}{0.200 \text{ ppm}} \times 100 = 100\%$$

*Net ppm