Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Mevinphos

MRID #: 417603-01

Matrix: Soil

Analysis: GC/FPD

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. 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.

ANALYTICAL METHOD

Determination of Alpha- and Beta-Mevinphos in Soil by Solvent Extraction and Gas Chromatography Using a Flame Photometric Detector

1. SCOPE AND APPLICATION OF THE METHOD

This is a gas chromatographic (GC) method applicable to the determination of Alpha- and beta-mevinphos in soils in the range of 0.01 to 5.0 μg/g (ppm). Limits of detection may vary between soils depending on the nature of interferences in the sample matrix and the specific instrumentation used. The method has been validated for one soil, a sandy loam from Madera, California, with relatively low organic matter content.

2. SUMMARY OF METHOD

Residues of Mevinphos are extracted from soil with acetonitrile. The extract is filtered and the water is removed by passing the extract through sodium sulfate. A portion of the extract is evaporated to near dryness and rediluted in acetone for quantitation. Analyte concentrations are determined by gas chromatography using a flame photometric detector. Results are calculated using linear regression from external standards. The validated sensitivity of the method is approximately 0.0101 ppm for both alpha- and beta-mevinphos.

3. DEFINITIONS

Laboratory duplicates -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

Laboratory reagent blank -- An extraction treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

Laboratory fortified control (spike) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the spike corrected for background concentrations.

Stock standard solution – A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

Primary dilution standard solution – A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

Calibration standard (CAL) – A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

Minimum quantifiable limit (MQL) – The lowest validated ppm level. For data reporting purposes, this is the lowest ppm value for which the method has been shown to be reliable.

4. APPARATUS AND EQUIPMENT

Apparatus Required (Items from other manufacturers may be used provided they are functionally equivalent).

1)	Gas Chromatograph:	Hewlett Packard Model 5890 Series II equipped with a flame photometric detector and 7673 autosampler.
2)	GC-Column:	J. and W. DB-17, megabore, 15 m x 0.53 mm x 1.0 µm film thickness.
3)	Integrator/Recorder:	Hewlett Packard Model HP 3392A.
4)	Balance:	Analytical, Electronic, Mettler AT200, precision ± 0.05 mg.
5)	Assorted Glassware:	500 ml screw cap Erlenmeyer flasks 500 ml mixing cylinders with vacuum adapters 125 ml flasks Class-A pipets Hamilton syringes Culture tubes with teflon-lined caps Etc.
6)	Assorted Supplies:	Polyethylene Büchner funnels Whatman, GF/A filter paper
7)	Platform Shaker:	Eberbach Corporation.

8) Rotary evaporators: Rinco rotors from Valley Electronics Corporation, Sargent Welch vacuum pump, and a warm water bath in which evaporation flasks can be partially submerged.

3. REAGENTS

A. Reagents Required (Items from other manufacturers may be used provided they are functionally equivalent).

1) Solvents: Distilled in Glass, Burdick and Jackson, Incorporated; acetonitrile (pesticide-grade) and acetone.

2) Reagents: A.C.S. grade, crystals, J.T. Baker, Incorporated; sodium sulfate and celite 545.

B. Standards Required

Analytical Standard: Known purity, supplied by Amvac Chemical Corporation, 4100 East Washington Boulevard, Los Angeles, CA 90023.

1) Alpha-mevinphos, 99.2%, Lot No. NS-50-50-1.

2) Beta-mevinphos, 97.5%, Lot No. NS-50-50-2.

C. Preparation of Solutions

1) Standard Solutions:

Tare a 10-ml class-A volumetric flask with a stopper. Into the flask weigh (to the nearest 0.1 mg) approximately 10 mg of alpha-mevinphos standard. Fill to the mark with acetone and mix well. Prepare a beta-mevinphos standard in the same manner.

2) Spiking Solutions:

Transfer 5.0 ml of alpha-mevinphos standard solution and 5.0 ml of beta-mevinphos standard solution to a 50.0 ml class-A volumetric flask and dilute to the mark with acetone. This solution yields a mixed spiking solution of approximately 100 µg/ml. Additional spiking solutions are prepared by making subsequent dilutions of the 100 µg/ml mixed spiking solution.

3) Gas Chromatography Standard Solutions:

Prepare a 100 µg/ml mixed solution as described in Section C.2. Subsequent dilutions of this mixed solution were prepared to yield GC standards at concentrations of 0.0250, 0.0500, 0.100, 0.500, 1.00, 2.50, and 5.00 µg/ml for both alpha- and beta-mevinphos.

6. SAMPLE PRESERVATION AND STORAGE

All samples received from the field are stored frozen at -20 ± 5°C prior to sample processing and analysis. Samples are ground in the presence of dry ice using a grist mill. After the dry ice is allowed to sublimate, the samples are transferred to high density linear polyethylene bottles and returned to the freezer pending analysis. All sample extracts are refrigerated at 4 ± 5°C until study completion and then discarded.

7. CALIBRATION

Inject 2 µl of each calibration (GC) standard and plot the peak height for each component versus its concentration to demonstrate linearity of response. Significant departure from linearity (a correlation coefficient of less than 0.995) indicates instrumental of operational difficulties which must be corrected before proceeding.

8. QUALITY CONTROL

The ability of the analyst to perform these procedures satisfactorily must be demonstrated by recovery tests before analysis of authentic samples is attempted. This is accomplished by conducting a method validation. In addition, at lease one recovery sample must be run concurrently with each batch of authentic samples to demonstrate that the overall operation of the procedure for that batch of samples was satisfactory. Recovery samples (also referred to as spikes or fortification samples) must yield recoveries ranging from 70 to 120%.

9. PROCEDURE

A. Analysis Procedure

1) Cut or chop soil samples into small pieces to obtain homogeneous samples.

2) Weigh 50 gm of representative sample into 500 ml screw cap Erlenmeyer flask.

3) Add 200 ml of acetonitrile and agitate at high speed on a platform shaker for 15 minutes.

4) Filter the extract through a Büchner funnel containing a Whatman GF/A filter paper and approximately 200 ml celite 545. The Büchner funnel is fitted with a vacuum adapter, containing approximately 25 grams sodium sulfate which is supported with glass wool. (See Figure 1.)

5) Adjust the volume to 500 ml with acetonitrile and mix thoroughly.

6) Remove a 50 ml aliquot from the mixing cylinder and place it in a 125 ml evaporation flask.

7) Concentrate the sample just to dryness using rotary evaporation.

8) Redissolve the residue in 1.0 acetone final volume for injection on the gas chromatograph.

9) Samples containing high residues may need further dilution with acetone so that the concentration of mevinphos in the diluted sample falls within the standard curve range.

10) Because no clean up procedure is used for this analysis, inspect the injector insert periodically for build-up.

B. Gas Chromatographic Conditions

Injector Temperature	= 200°C
Detector Temperature	= 250°C
Oven Temperature	= 145°C
Gas Flow Rates:	Nitrogen = 10ml/min (column)
	25 ml/min (make-up)
	Air = 100 ml/min
	Hydrogen = 75 ml/min
	Alpha-mevinphos = ~6.15 min
	Beta-mveinphos = 7.00 min

C. Automated Gas Chromatographic Analysis

Begin the automated GC set with at least two standards. Follow these standards with unknown (authentic) samples and standards arranged on the autosampler tray so that no more than 10 unknowns are injected without a standard injection. If a sample peak height exceeds the peak height of the most concentrated standard in the standard curve, dilute the sample solution with acetone so that its peak height will fall within the standard curve and reinject; record the dilution factor for use in calculations as described in Section 11 below.

11. CALCULATIONS

Calculate the concentrations of alpha- and beta-mevinphos as follows:

1) Compile the concentration of all standards injected (independent variable, x-axis and their corresponding peak heights (dependent variable, y-axis).

2) Use a calculator/computer and linear regression to determine the slope and correlation coefficient of standard concentration versus peak height, setting the y-intercept to zero. Back-calculate analyte concentrations using the following equation:

$$\text{ppm } (\mu g/g) = \frac{Ht\text{-}h}{m} \times \frac{V}{W} \times F \times \frac{AV}{SV}$$

Where:

Ht = peak height of sample
b = y-intercept of the linear regression line (b=0 for linear regression/forced through zero)
m = slope of the linear regression line
V = final volume for GLC analysis (in ml)
W = amount of sample extracted (in gm)
F = factor for conversion to desirable units of measurable
AV = aliquo. volume
SV = adjusted sample volume following extraction

NOTE: The Lotus 1-2-3 computer program automatically calculates the slope, y-intercept, and correlation coefficient. From the curve equation, concentrations of sample residues (µg/g) are automatically extrapolated.

An example calculation for alpha-mevinphos in sample EF-90-305-V119 is presented below:

Standard curve equation: y = 133099 x + 0
Where y is equivalent to peak height units and x is concentration in µg/ml
Peak height of sample: 6869
µg/ml equivalents from curve: 0.0516

$$\mu g/g\ (ppm) = \frac{(0.0516\ \mu g/ml)\ (500\ ml)\ (1\ ml)}{(50.353\ g)\ \ (50\ ml)\ (.9641)} = 0.445\ ppm\ alpha\text{-}mevinphos$$

12. PRECISION AND ACCURACY

Tables I and II present typical recoveries from fortified controls (spikes). Table I summarizes the results of the method validation from the San Joaquin Valley site. Recoveries for alpha-mevinphos were 96.7 ± 6.94% and 91.9 ± 8.38% for beta-mevinphos. Table II shows recoveries from spikes run during authentic sample analysis. Average recoveries for alpha-mevinphos were 85.6 ± 10.4% and 94.7 ± 5.96%. In beta-mevinphos, average recoveries were 80.4 ± 11.8% and 94.8 ± 6.75%.

13. REFERENCES

This method was developed from a CDFA multi-residue screening method presented in Appendix I.

TABLE I

SUMMARY OF VALUES FOR MEVINPHOS SOIL METHOD VALIDATION FOR THE SAN JOAQUIN VALLEY SITE

ALPHA MEVINPHOS		BETA MEVINPHOS	
SAMPLE	% RECOVERY	SAMPLE	% RECOVERY
REAGENT BLANK	ND	REAGENT BLANK	ND
CONTROL A	ND	CONTROL A	ND
CONTROL B	ND	CONTROL B	ND
0.0100 PPM A	86.3%	0.0100 PPM A	81.0%
0.0100 PPM B	90.0%	0.0100 PPM B	82.8%
0.0100 PPM C	101%	0.0100 PPM C	94.8%
0.500 PPM A	92.6%	0.500 PPM A	89.0%
0.500 PPM B	101%	0.500 PPM B	97.2%
5.00 PPM A	104%	5.00 PPM A	100%
5.00 PPM B	102%	5.00 PPM B	98.0%
MEAN	96.8%		91.8%
SD	6.81%		7.63%
COV	7.04%		8.31%

ND IS NOT DETECTABLE

TABLE II

SUMMARY OF SPIKE RECOVERIES FOR ANALYSIS OF SOIL FROM SAN JOAQUIN VALLEY DISSIPATION SITE

	0.01 ALPHA 5.0		0.01 BETA 6.0	
SET #	LOW SPIKE *	HIGH SPIKE **	LOW SPIKE *	HIGH SPIKE **
4	76.6%	102%	73.6%	99.2%
7	96.0%	94.4%	77.0%	90.8%
14	87.1%	79.2%	85.9%	78.4%
16	35.8%	95.6%	75.6%	91.2%
17	83.8%	94.3%	83.6%	96.6%
18	89.7%	96.6%	87.5%	100%
19	117%	96.6%	112%	103%
20	86.7%	94.7%	81.2%	96.2%
21	86.9%	94.7%	78.2%	97.0%
22	82.4%	97.8%	71.9%	97.8%
26	92.9%	93.9%	84.4%	93.1%
27	91.9%	95.8%	79.0%	95.4%
29	83.6%	90.7%	73.2%	88.3%
30	89.3%	88.7%	86.9%	85.9%
31	83.6%	94.3%	83.6%	94.7%
32	93.3%	89.1%	93.7%	89.5%
33	83.2%	98.2%	80.0%	100%
34	84.2%	91.5%	90.3%	95.8%
35	78.0%	95.4%	80.8%	88.7%
35A	91.1%	85.9%	87.3%	89.1%
37	90.1%	92.7%	84.4%	96.2%
38	94.1%	97.0%	89.3%	100%
39	85.7%	99.4%	80.2%	105%
40	83.8%	101%	77.2%	105%
41	67.5%	92.3%	63.8%	89.9%
42	88.3%	89.9%	76.2%	88.7%
43	75.4%	99.1%	74.3%	88.7%
44	77.4%	97.0%	68.5%	97.4%
45	72.3%	91.9%	64.4%	92.3%
45A	76.2%	99.4%	70.9%	105%
47	75.0%	96.6%	72.9%	96.2%
48	82.0%	93.9%	69.5%	95.0%
50	95.8%	111%	82.0%	94.3%
62		105%		109%
MEAN	85.7%	94.9%	80.1%	95.0%
SD	3.97%	5.61%	9.26%	6.53%
C.O.V.	10.5%	5.91%	11.6%	6.87%

* LOW SPIKE = 1 PPM ** HIGH SPIKE = 5 PPM