Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Metaldehyde

MRID #: 422870-01

Matrix: Soil

Analysis: GC/NPD

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EN-CAS Method No. EMC-2/91

Analytical Method for the Determination of Metaldehyde in Soil

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TITLE: Analytical Method for the Determination of Metaldehyde in Soil	QA APPROVAL [signature] MGMT APPROVAL [signature] 4/08/93	

1.0 INTRODUCTION

1.1 Scope

This method is used for the determination of metaldehyde residues in soil samples from locations in California. The method uses a derivatization of metaldehyde to acetaldehyde 2,4-dinitrophenylhydrazone (2,4-DNPH) as the analytical approach. A method from the Research and Consulting Company AG entitled Determination of Metaldehyde Residues in Plant Material (Reference 3) was used in developing this method. The limit of quantitation (LOQ) is 0.02 ppm (µg/g) metaldehyde. Method validation results from EN-CAS report 90-0035 LO Determination of Metaldehyde Residues in/on Soils From a Terrestrial Dissipation Study of Metaldehyde in the San Joaquin Valley of California, are included in this report (see Table I). See Figure 1 for a flowchart of the method.

1.2 Principle

Metaldehyde is extracted from soil by shaking with dichloromethane (DCM) that has been pre-washed with 2% aqueous sodium bisulfite to remove traces of the contaminant, acetaldehyde. An aliquot of the DCM extract is washed with 2% aqueous sodium bisulfite to remove extracted aldehydes which may cause GC interferences after derivatization. After washing, the DCM phase is derivatized by shaking with a 0.5% solution of 2,4-dinitrophenylhydrazine (2,4-DNP) in 6N HCl (prior to use, the derivatization reagent is pre-washed with DCM to remove traces of acetaldehyde

1.2 Principle (continued)

2,4-DNPH which may be present as a contaminant). Under the acidic derivatization conditions, the metaldehyde is converted to acetaldehyde which then dissolves in the aqueous phase and reacts with the 2,4-DNP to form acetaldehyde 2,4-DNPH. The acetaldehyde 2,4-DNPH is DCM-soluble and is therefore returned to the DCM phase as it is formed during the derivatization-shaking process. The reaction mixture is transferred to a separatory funnel and the organic phase containing the derivative is drained back into the reaction vessel (the aqueous phase is discarded). The organic phase is returned to the separatory funnel, washed with 6N HCl, followed by a wash with water (HPLC grade). The sample is then filtered through a pad of anhydrous sodium sulfate and reduced to ~5 mL by vacuum rotary evaporation at a bath temperature of 30°C - 35°C. To remove the last traces of DCM, ethyl acetate is added to the sample and the sample is evaporated to dryness using vacuum rotary evaporation with a bath temperature of 30°C - 35°C. The sample extract is adjusted to an appropriate final volume. Gas chromatographic separation is accomplished with a capillary DB-17 column. Analyte detection is obtained using an alkali flame nitrogen/phosphorus (N/P) detector.

2.0 APPARATUS

All equipment and apparatus may be replaced by equivalent items from alternate sources.

NOTE: Prior to use, all labware should be rinsed with DCM (which has been pre-washed with sodium bisulfite). Neither acetone nor methanol should be used to rinse glassware. Acetone reacts with the 2,4-DNP derivatizing agent giving rise to a potential interference. Methanol contains small amounts of acetaldehyde which can also interfere in the metaldehyde analyses.

2.1 French square bottles, 4-oz and 32-oz

2.2 Caps, polyethylene-lined, for French square bottles

2.3 Separatory funnels, 250-mL

2.0 APPARATUS (continued)

2.4 Erlenmeyer flasks, 250-mL, with 24/40 ground glass fittings

2.5 Stoppers, ground glass, 24/40

2.6 Volumetric flasks, 100 mL, for preparing analytical standards

2.7 Powder funnels, glass, 4-inch diameter

2.8 Disposable Pasteur pipettes, 23-cm

2.9 Scintillation vials, 20-mL

2.10 GC vials, 2-mL

2.11 Mechanical Shaker (G10 Gyrotory)

2.12 Rotary Evaporator, cold fingers (Buchi Rotovapor, model #RE111)

2.13 Top loading balance, (Fisher Scientific, Model XT-3KD)

2.14 Mettler analytical balance capable of 5 decimal accuracy, for weighing analytical standards

3.0 REAGENTS

3.1 Dichloromethane (DCM), pesticide grade.

NOTE: Just prior to use (on the same day), wash the DCM with 2% (w/v) sodium bisulfite solution. This is accomplished by partitioning the DCM with 5 parts 2% aqueous sodium bisulfite to 1 part DCM.

3.2 Ethyl acetate, pesticide grade

3.3 Methanol, Fisher Scientific, Optima grade

NOTE: All grades of methanol are contaminated with small amounts of acetaldehyde. The purest grade of methanol available should be used.

3.4 Hydrochloric acid, ACS Reagent grade

3.5 Derivatizing reagent, 0.5% solution of 2,4-dinitrophenylhydrazine in 6N HCl (prepared daily)

3.0 REAGENTS (continued)

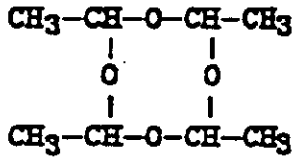
NOTE: Prepare derivatizing reagent by weighing 0.5 g of 2,4-dinitrophenylhydrazine per 100 mL of 6N HCl (diluted from 12N HCl). Warm, if necessary, to dissolve. Wash the reagent with 2½ times its volume of pre-washed DCM on the day of use.

3.6 Sodium sulfate (Na_2SO_4), anhydrous, ACS certified, heated in a muffle furnace at 600°F for 2 hours

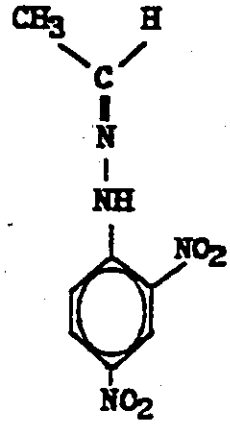
3.7 Sodium bisulfite, ACS certified

3.8 B & J bottled water, HPLC grade

4.0 TEST SUBSTANCES



Metaldehyde
($C_8H_{16}O_4$)
MW = 176.2



Acetaldehyde 2,4-dinitrophenylhydrazone
(2,4-DNPH) MW = 224.2

4.0 TEST SUBSTANCES (continued)

$$C_8H_{16}O_4 \xrightarrow{H^+} 4\ CH_3CHO$$

metaldehdye ——————> acetaldehyde

$$CH_3CHO \xrightarrow{\text{DNPH reagent } H^+} CH_3CH{=}N{-}NH{-}C_6H_3(NO_2)_2$$

acetaldehyde ——————> acetaldehyde 2,4-DNPH

5.0 PREPARATION OF ANALYTICAL STANDARDS

5.1 Fortification Standards

Weigh 100 mg (active ingredient) of the test substance, metaldehyde, using an analytical balance into a 100-mL volumetric flask. Dissolve and dilute to volume with methanol to prepare a 1000 µg/mL stock solution. [NOTE: All grades of methanol are contaminated with small amounts of acetaldehyde. Use a grade which minimizes the acetaldehyde concentration. Fisher Optima grade specifies a maximum of 0.001% acetaldehyde, although in our experience the amount present in typical lots appears to be significantly less than this.] Serially dilute the 1000 µg/mL stock solution in methanol to prepare 100 µg/mL and 10 µg/mL standard solutions. Use these solutions to fortify soil control samples in order to monitor procedural recovery. The stock standard solution is stable for approximately 6 months. [NOTE: Store all standard stock solutions in a freezer at a temperature of -10°C to -17°C.]

5.2 Gas Chromatographic Standards

Gas chromatographic standards are prepared by taking known quantities of metaldehyde through the 2,4-DNP derivatizing procedure. In this way, the reagent background in the standard is sufficiently similar to that in the samples to permit direct GC comparison of standards and samples. Note that experiments in our laboratory indicate that the derivatizing reagent blank substantially enhances the capillary GC-N/P response to acetaldehyde 2,4-DNPH. Removal of the reagent blank components from the acetaldehyde 2,4-DNPH by purification procedures other than those used to prepare the corresponding soil samples, will lead to erroneously low responses for the GC standards and therefore, incorrect elevation of residues in the soil samples. For this reason, the GC standards are prepared as mentioned above.

Using the 1000 µg/mL metaldehyde stock solution prepared in Section 5.1 above, dilute with sufficient pre-washed DCM to obtain a 1 µg/mL solution. To individual 25-mL aliquots of pre-washed DCM contained in separatory funnels, add the following volumes of the 1 µg/mL metaldehyde solution: 0.1 mL, 0.2 mL, 0.5 mL and 1 mL. Higher concentrations of standards are prepared directly from the 1000 µg/mL metaldehyde stock solution in methanol and the following volumes added: 0.01 mL, 0.025 mL, 0.05 mL, 0.1 mL and 0.2 mL. When carried through the derivatizing procedure and recovered in 10 mL of ethyl acetate, these standards will contain acetaldehyde 2,4-DNPH equivalent to the following metaldehyde concentrations: 0.01 µg/mL, 0.02 µg/mL, 0.05 µg/mL, 0.10 µg/mL, 1.0 µg/mL, 2.5 µg/mL, 5.0 µg/mL, 10 µg/mL and 20 µg/mL. Fresh standards are made at least weekly. [NOTE: Store all standard solutions in a refrigerator at a temperature of 1°C to 3°C.]

6.0 ANALYTICAL PROCEDURES

6.1 Extraction

NOTE: Pre-wash the dichloromethane by partitioning with 5 parts 2% aqueous sodium bisulfite to 1 part DCM. Discard the 2% aqueous sodium bisulfite.

6.1.1 Weigh 100 g of soil (processed according to EN-CAS SOP III-5.9, see Appendix A) into a 32-oz French square bottle. Make appropriate laboratory fortifications with the metaldehyde stock solution prepared in Section 5.1. Minimum volumes (usually less than or equal to 1 mL) of the methanol fortification solution are used in order to minimize potential interferences from the traces of acetaldehyde in the methanol. Allow solvent from the fortification to evaporate for approximately 20-30 minutes.

6.1.2 Add 250 mL of DCM (pre-washed with 2% aqueous sodium bisulfite; see NOTE above) to the French square bottle.

6.1.3 Add 500 g of anhydrous sodium sulfate to the DCM/soil mixture. Cap the bottle using a cap with a polyethylene liner and place plastic tape on the outside to prevent leakage.

6.1.4 Place the bottle on its side in the mechanical shaker and shake vigorously (approximately 200 rpm) for 15 minutes on one side. Turn the bottle to the opposite side and continue shaking for an additional 15 minutes.

6.1.5 Remove the bottle from the shaker, place it upright and let the sample settle for at least 15 minutes.

6.2 Partition and Derivatization

6.2.1 Transfer a 25-mL sample aliquot to a 250-mL separatory funnel.

6.2.2 Wash the DCM aliquot by shaking with 10 mL of 2% aqueous sodium bisulfite solution. Allow the phases to separate. [NOTE: The metaldehyde residues will remain in the organic phase.]

6.2 Partition and Derivatization (continued)

6.2.3 Drain the organic phase into a 4-oz French square bottle. Discard the remaining aqueous wash. Add 10 mL of derivatizing reagent (0.5% solution of 2,4-DNP in 6N HCl - see Section 3.5).

NOTE: The derivatizing reagent must be washed with DCM (pre-washed with 2% aqueous sodium bisulfite) prior to use in order to remove acetaldehyde 2,4-DNPH contamination that may be present. This is accomplished by partitioning the derivatizing agent with 2.5 times its volume of pre-washed DCM (see Section 6.1), then discarding the DCM. The derivatizing reagent is prepared daily.

6.2.4 Cap the bottle securely using a cap with a polyethylene liner and mechanically shake (~200 rpm) the sample for 20 minutes.

6.2.5 Transfer the reaction mixture back to the 250-mL separatory funnel. [NOTE: The organic phase will contain the acetaldehyde 2,4-dinitrophenylhydrazone derivative.]

6.2.6 Drain the organic phase back into the reaction vessel (the 4-oz French square bottle) and discard the aqueous phase.

6.2.7 Return the organic phase to the separatory funnel. Wash the organic phase by shaking with 2 x 20 mL of 6N HCl. Discard both acid washes.

6.2.8 Wash the organic phase again by shaking with 2 x 20 mL of HPLC grade water. Discard both water washes.

6.3 Filtration and Evaporation

6.3.1 Filter the sample through a pad (approximately 50 g) of anhydrous sodium sulfate into a 250-mL Erlenmeyer flask with a ground glass neck. Rinse the sodium sulfate pad with 25 mL of DCM (pre-washed with 2% aqueous sodium bisulfite), combining the rinse with the filtrate.

6.3 Filtration and Evaporation (continued)

6.3.2 Evaporate the sample to approximately 5 mL under vacuum rotary evaporation using a bath temperature of 30°C - 35°C.

6.3.3 Add 25 mL of ethyl acetate and evaporate to dryness using vacuum rotary evaporation at a temperature of 30°C - 35°C.

6.3.4 Dissolve the sample extract in an appropriate final volume (usually 10 mL) with ethyl acetate. Proceed to gas chromatographic analysis.

6.4 Gas Chromatographic Determination

Use a 30 m x 0.32 mm, 0.25-µm film thickness, capillary DB-17 column to achieve gas chromatographic separation. Use a Hewlett-Packard Model 5890-A Gas Chromatograph (or equivalent) with an alkali flame, nitrogen/phosphorus (N/P) detector to provide adequate sensitivity and selectivity. Gas chromatographic conditions are listed in Section 7.0 of this method.

6.5 Safety Precautions

Safety goggles must be worn when working with the high concentrations of HCl used in this method. Work should be done in a fume hood to minimize exposure to the analytes, HCl fumes and organic solvents. The chemical waste generated in this procedure should be segregated from any oxidizing agents.

6.6 Limit of Quantitation

For the soil types validated herein, this method is proven effective to a LOQ of 0.02 ppm metaldehyde. Adjust the instrument sensitivity, GC calibration standards and final sample volumes to allow detection of metaldehyde at 50% of the LOQ.

6.7 Time Required for Analysis

An experienced technician can process a set of approximately 12 samples (including controls and recoveries), and prepare them for injection on the gas chromatograph in approximately one 8-hour day. An additional day is required for reinjections and for annotating and calculating the data.

6.8 Interference and Potential Problems

There are many ambient sources of acetaldehyde in the laboratory environment. Therefore, extensive care should be taken to prevent ambient acetaldehyde from interfering in the method. Some of the precautions are outlined below.

6.8.1 Glasswashing and Pre-cleaning Procedures

After normal glassware washing has occurred, wash all glassware used in this procedure with DCM (pre-washed with 2% aqueous sodium bisulfite).

6.8.2 Solvent Pre-washing

Pre-wash all of the DCM used in this procedure with 2% aqueous sodium bisulfite.

6.8.3 Derivatizing Reagent Pre-washing

The derivatizing reagent (0.5% solution of 2,4-dinitrophenylhydrazine) is pre-washed with DCM (which has been pre-washed with 2% aqueous sodium bisulfite).

6.8.4 Chromatographic Interferences

After the analyte has eluted from the GC, the column temperature is raised to 275°C to burn off any long retention time interferences before the next injection.

6.8 Interference and Potential Problems (continued)

6.8.5 Matrix and Solvent Effects During Gas Chromatography

The reagent background which remains in the derivatized sample at the time of gas chromatography analysis has an enhancing effect on the acetaldehyde 2,4-DNPH signal during capillary GC-N/P analysis. For accurate determinations of metaldehyde, it is therefore critical that the standards be derivatized and prepared in the same manner as the soil extracts.

6.8.6 Instrument Maintenance

Deterioration of chromatography and baseline instability may be seen after as few as 50 injections. When this is observed, the following maintenance functions are performed: the inlet liner is replaced, the entire injection port is cleaned (and the seals replaced), and approximately 0.5 to 1 meter of the front portion of the column is removed. If these maintenance activities do not improve the chromatography, then the N/P detector bead should be replaced.

7.0 GAS CHROMATOGRAPHIC ANALYSIS

7.1 Description and Typical Operating Conditions

Instrument: Hewlett-Packard Model 5890-A Gas Chromatograph with an alkali flame, nitrogen/phosphorus (N/P) detector equipped with a 7673A Automatic Sampler. Data is collected and processed with a Hewlett-Packard 3396A Integrator.

Column: DB-17, 30 m x 0.32 mm (J & W Scientific), 0.25-µm film thickness

Gases:

Carrier:	He	4.80 mL/min.
Detector:	H_2	4.43 mL/min.
	Air	84.8 mL/min.
	Aux He	25.5 mL/min.

7.1 Description and Typical Operating Conditions (continued)

Injection: 1 µL, splitless

Temperatures:

Injector:	250°C
Detector:	275°C
Column Temperature Program	
Initial Oven Temperature	= 50°C
Initial Time	= 1.5 min.
Ramp A	= 40°/min.
Oven Temperature	= 225°C
Time	= 7.0 min.
Ramp B	= 40°/min.
Oven Temperature	= 275°C
Final Time	= 10 min.

Typical Retention Time:

Isomer # 1 = ~ 11.0 min.
Isomer # 2 = ~ 11.3 min.

Typical Integrator Parameters: Hewlett-Packard 3396A Integrator

```
RUN PARAMETERS
 ZERO  =  0
 ATT 2^= 1
 CHT SP= 2  (cm/min)
 AR REJ= 0
 THRSH = -2
 PK WD = .03

TIMETABLE EVENTS
 TIME  0.000 INTG#  =  8
 TIME  0.000 INTG#  =  2
 TIME  0.000 INTG#  =  9
 TIME 10.500 CHT SP =  2.0
 TIME 10.510 INTG#  = -9
 TIME 10.520 ZERO   = 20
 TIME 10.530 ATT 2^ =  1
 TIME 11.700 STOP
```

```
INTEGRATOR DEFINITIONS
 0. SET BASELINE NOW
 1. SET BASELINE NEXT VALLEY
 2. SET BASELINE ALL VALLEYS
 3. SKIM FROM NEXT PEAK
 4. DISABLE AUTO-TANGENT SKIMMING
 5. EXTEND BASELINE HORIZONTALLY
 6. MEASURE AND UPDATE THRESHOLD
 7. TURN OFF RETENTION TIME LABELING
 8. TURN ON START/STOP MARKS
 9. TURN OFF INTEGRATION
10. INCREMENT THRESHOLD
11. INVERT NEGATIVE PEAK
12. CLAMP NEGATIVE PEAKS
13. SHOW EV11, EV12
14. START PEAK SUM WINDOW
```

7.2 Calibration

In order to bracket a wide range of metaldehyde concentrations, two standard curves are used for quantitation. Assuming a 10 mL final extract volume, the lower range curve (0.01 to 0.10 µg/mL) covers metaldehyde soil concentrations from 0.02 to 0.1 ppm. The higher range curve (0.1 µg/mL to 20 µg/mL) covers metaldehyde soil concentrations between 0.1 and approximately 20 ppm. The demonstrated linear response range for acetaldehyde 2,4-DNPH is from 0.01 µg/mL to 20 µg/mL on the HP 5890 N/P detector. Sample residue values and fortification values which range above the 0.1 µg/mL standard must be injected within the higher range standard curve (0.1 µg/mL to 20 µg/mL). This approach allows reagent background in the samples and standards to remain constant. Only in rare cases would metaldehyde residues in the soil exceed 20 ppm after normal application.

Use the metaldehyde GC calibration standards that were prepared in the method (Section 5.2) in concentrations ranging from 0.01 µg/mL to 0.10 µg/mL or from 0.10 µg/mL to 20 µg/mL to calibrate the instrument. Inject appropriate standards at the beginning of the run, after approximately every 2 or 3 samples throughout the run, and at the end of the run. A linear regression function is generated using the resulting summation peak height of the two isomers, see Section 8.0, (obtained from the integrator after subtraction of the reagent blank contribution) vs. nanograms injected. The correlation coefficient for the line should generally be equal to or greater than 0.990. The sample nanograms found are determined by inserting the summation peak height value (corrected for the reagent blank) of the two isomers into the standard curve linear regression equation.

7.3 GC Analyses of Samples

The peak heights of the calibration standards are corrected for the concurrent reagent blank. Additionally, the peak heights of the control and treated samples are each corrected for the concurrent reagent blank. Any remaining control contribution is subtracted from the fortified recovery sample results. No correction for control is made for treated residue samples.

8.3 Calculation of ppm Found

$$\text{ppm found} = \frac{\text{ng found}}{\text{ng-equiv. injected}}$$

8.4 Calculation of Soil Moisture

Determine the percent of moisture in the soil by weighing 10 grams of soil in duplicate, drying overnight at an oven temperature of 110°C, and reweighing the soil. The average of the duplicate soil moistures is to be used in the residue calculation.

Percent moisture in a soil sample:

$$\frac{\text{wet wt.} - \text{dry wt.}}{\text{wet wt.}} \times 100 = \% \text{ moisture}$$

8.5. Calculation of Soil Residues on Dry Weight Basis

$$\text{ppm dry} = \frac{\text{ppm wet}}{(1 - \text{decimal \% moisture})}$$

8.6 Calculation of Percent Recovery

When calculating percent recovery of a laboratory fortification, use the following ppm subtraction calculation if there is control contribution present.

$$\text{ppm (corrected)} = \text{ppm (sample)} - \text{ppm (control)}$$

8.6 Calculation of Percent Recovery (continued)

$$\% \text{ Recovery} = \frac{\text{ppm found (corrected)}}{\text{fortification level (ppm)}}$$

8.7 Example Calculation

Example: Set HW # 2, run 37237 EN-CAS Sample ID: EX1890-S2

Net sample counts = 4509 sample counts - 1026 reagent blank counts = 3483 counts

$$\text{ng found} = \frac{3483 \text{ counts} - (-473.83 \text{ counts})}{151022.9 \text{ counts}} = 0.0262 \text{ ng}$$

$$\text{ng equiv. injected} = \frac{200 \text{ g} \times 25 \text{ mL} \times 1.0 \text{ µL} \times 1000 \text{ ng/g}}{250 \text{ mL} \times 10 \text{ mL} \times 1.0 \times 1000 \text{ µL/mL}} = 1.0 \text{ ng equiv.}$$

$$\text{ppm found} = \frac{0.0262 \text{ ng}}{1.0 \text{ ng equiv.}} = 0.0262 \text{ ppm}$$

ppm (corrected) = 0.0262 ppm (sample) - 0.0029 ppm (control) = 0.0233 ppm

$$\% \text{ Recovery} = \frac{0.0233 \text{ ppm (corrected)}}{0.02 \text{ ppm added}} \times 100 = 117\%$$

9.0 VALIDATION RESULTS

See Table I in this report.

9.1 Statistical Method

The mean recoveries and standard deviations are calculated from the validation data and appear in the validation tables included in this method. The standard deviation is calculated using the following equation:

$$SD_{(n-1)} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

where the sum of the squares of the individual deviations from the mean $(x_i - \bar{x})$ is divided by one less than the total number of measurements in the set, n-1 (when the total number of measurements is less than 30).

9.2 Discussion of Validation Results

Recovery means and standard deviations calculated for the method validation in 0-6", 6-12" and 12-18" California soil indicate a reliable method for the determination of metaldehyde as 2,4-DNPH by gas chromatography.

In spite of the extensive provisions in the method for minimizing background from ambient acetaldehyde, a small but measurable acetaldehyde background appears in the reagent blank. Small variations in this blank sometimes result in the appearance of somewhat elevated recoveries (~150%) at the method LOQ.

10.0 REFERENCES

1. EPA Pesticide Guidelines Subdivision O, Series 171-4 (c)(4).

2. U.S. Environmental Protection Agency, August 17, 1989, Pesticide Programs; Good Laboratory Practice Standards; Final Rule (40 CFR. Part 160). Federal Register Vol. 54: 34052-34074.

3. Research and Consulting Company AG Method entitled Determination of Metaldehyde Residues in Plant Material.

TABLE I

Metaldehyde in San Joaquin California Soil
Method Validation Results
(0-6")

EN-CAS ID #	Set #	Field ID #	Soil Depth	Date Extracted	Date Analyzed	Fortification Level (ppm)	Metaldehyde[a] % Recovered or ppm (mg/g) Found
R-BLK/1	MV1	-	0-6"	10/24/91	11/17/91	-	<0.02
EJ1889-C1	MV1	EF90303-21	0-6"	10/24/91	11/17/91	-	<0.02
EJ1889-C2	MV1	EF90303-21	0-6"	10/24/91	11/17/91	-	<0.02
EJ1889-S1	MV1	EF90303-21	0-6"	10/24/91	11/17/91	0.02	158
EJ1889-S2	MV1	EF90303-21	0-6"	10/24/91	11/17/91	0.02	131
EJ1889-S3	MV1	EF90303-21	0-6"	10/24/91	11/17/91	0.10	139
EJ1889-S4	MV1	EF90303-21	0-6"	10/24/91	11/17/91	0.10	122
EJ1889-S5	MV1	EF90303-21	0-6"	10/24/91	11/17/91	1.0	99[b]
EJ1889-S6	MV1	EF90303-21	0-6"	10/24/91	11/17/91	1.0	119

[a] Detected as 2,4-dinitrophenylhydrazone and reported in metaldehyde equivalents.
[b] Sample spilled during processing.

TABLE I (continued)

Metaldehyde in San Joaquin California Soil
Method Validation Results
(6-12")

EN-CAS ID #	Set #	Field ID #	Soil Depth	Date Extracted	Date Analyzed	Fortification Level (ppm)	Metaldehyde[a] % Recovered or ppm (µg/g) Found
R-BLK/1	MV2	-	6-12"	10/25/91	11/15/91	-	<0.02
R-BLK/1	MV2	-	6-12"	10/25/91	11/15/91	-	<0.02
EJ1890-C1	MV2	EF90303-22	6-12"	10/25/91	11/15/91	-	<0.02
EJ1890-C2	MV2	EF90303-22	6-12"	10/25/91	11/15/91	-	<0.02
EJ1890-S1	MV2	EF90303-22	6-12"	10/25/91	11/15/91	0.02	118
EJ1890-S2	MV2	EF90303-22	6-12"	10/25/91	11/15/91	0.02	109
EJ1890-S3	MV2	EF90303-22	6-12"	10/25/91	11/15/91	0.10	104
EJ1890-S4	MV2	EF90303-22	6-12"	10/25/91	11/15/91	0.10	134
EJ1890-S5	MV2	EF90303-22	6-12"	10/25/91	11/15/91	1.0	117
EJ1890-S6	MV2	EF90303-22	6-12"	10/25/91	11/15/91	1.0	114

[a] Detected as 2,4-dinitrophenylhydrazone and reported in metaldehyde equivalents.

TABLE I (continued)

Metaldehyde in San Joaquin California Soil
Method Validation Results
(12-18")

EN-CAS ID #	Set #	Field ID #	Soil Depth	Date Extracted	Date Analyzed	Fortification Level (ppm)	Metaldehyde[a] % Recovered or ppm (µg/g) Found
R-BLK/1	MV3	-	12-18"	10/28/91	11/17/91	-	<0.02
R-BLK/2	MV3	-	12-18"	10/28/91	11/17/91	-	<0.02
EJ1891-C1	MV3	EF90303-23	12-18"	10/28/91	11/17/91	-	<0.02
EJ1891-C2	MV3	EF90303-23	12-18"	10/28/91	11/17/91	-	<0.02
EJ1891-S1	MV3	EF90303-23	12-18"	10/28/91	11/17/91	0.02	101
EJ1891-S2	MV3	EF90303-23	12-18"	10/28/91	11/17/91	0.02	91
EJ1891-S3	MV3	EF90303-23	12-18"	10/28/91	11/17/91	0.10	79
EJ1891-S4	MV3	EF90303-23	12-18"	10/28/91	11/17/91	0.10	84
EJ1891-S5	MV3	EF90303-23	12-18"	10/28/91	11/17/91	1.0	68
EJ1891-S6	MV3	EF90303-23	12-18"	10/28/91	11/17/91	1.0	94

[a] Detected as 2,4-dinitrophenylhydrazone and reported in metaldehyde equivalents.

FIGURE 1

Flowchart of Analytical Method ENC-2/91

Analytical Method for the Determination of Metaldehyde in Soil

Extract metaldehyde by adding DCM (pre-washed with 2% aqueous sodium bisulfite) and solid anhydrous sodium sulfate to the soil sample and mechanically shaking.

▼

Derivatize an aliquot of the DCM extract by mechanically shaking with 2,4-dinitrophenylhydrazine in 6N HCl (pre-washed with DCM)

▼

Transfer the reaction mixture to a separatory funnel and (after discarding the aqueous phase) wash the organic phase with acid (discard acid washes).

▼

Wash the organic phase with water (discard water washes).

▼

Filter the sample through anhydrous sodium sulfate.

▼

Evaporate the sample to a small volume using rotary evaporation.

▼

Add ethyl acetate and evaporate to dryness.

▼

Reconstitute the residue with ethyl acetate to an appropriate final volume.

▼

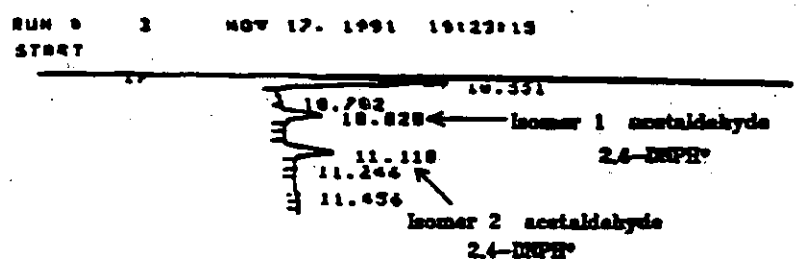
Analyze on a gas chromatograph using N/P detection and a capillary DB-17 column.

FIGURE 2

Typical Chromatogram

Reagent Blank

Attenuation = 2^4



Metaldehyde Equivalents Found: <0.02 ppm (0.0061 ppm)
GC run # 37243, set MV-1, dated 11/17/91

* Expressed as metaldehyde equivalents

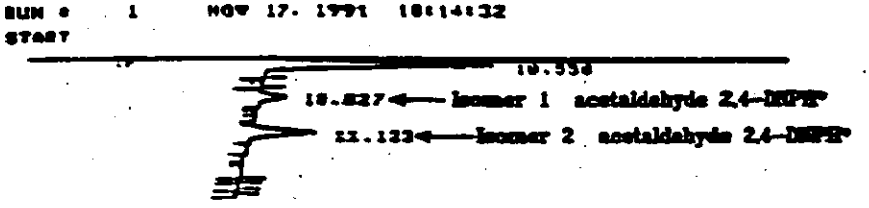
FIGURE 3

Typical Chromatogram

GC Standard

0.01 µg/mL Acetaldehyde 2,4-Dinitrophenylhydrazone (2,4-DNPH) as Metaldehyde Equivalents

Attenuation = 2^2



0.01 ng injected
GC run # 37243, set MV-1, dated 11/17/91

* Expressed as metaldehyde equivalents

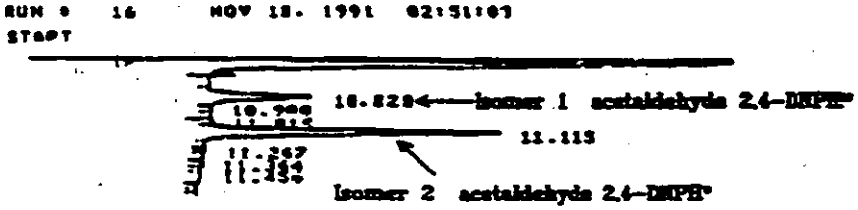
FIGURE 4

Typical Chromatogram

GC Standard

0.05 µg/mL Acetaldehyde 2,4-Dinitrophenylhydrazone (2,4-DNPH) as Metaldehyde Equivalents

Attenuation = 2^2



0.05 ng injected
GC run # 37243, set MV-1, dated 11/18/91

* Expressed as metaldehyde equivalents

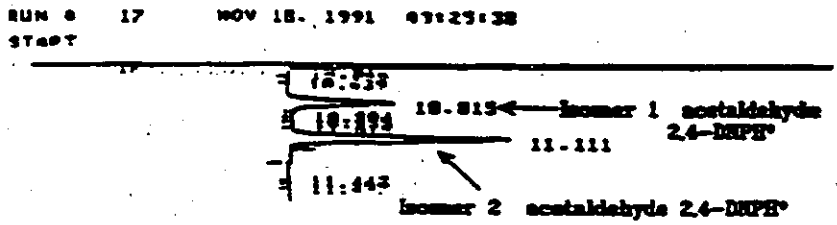
FIGURE 5

Typical Chromatogram

GC Standard

1.0 µg/mL Acetaldehyde 2,4-Dinitrophenylhydrazone (2,4-DNPH) as Metaldehyde Equivalents

Attenuation = 2'



1.0 ng injected
GC run # 37243, set MV-1, dated 11/18/91

* Expressed as metaldehyde equivalents

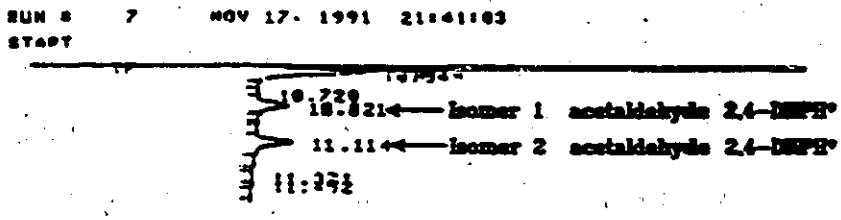
FIGURE 6

Typical Chromatogram

Soil Control

(0-6")

Attenuation = 2^2



EN-CAS Sample ID #: EJ1889-C2
Metaldehyde Equivalents Found: <0.02 ppm (0.0041 ppm)
GC run # 37243, set MV-1, dated 11/17/91

* Expressed as metaldehyde equivalents

FIGURE 7

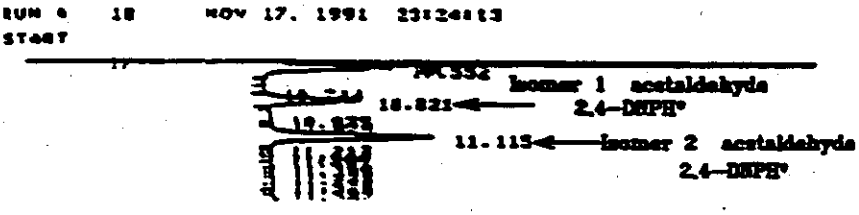
Typical Chromatogram

Soil Control + 0.02 ppm Metaldehyde

(0-6")

Low Fortification

Attenuation = 2^3



EN-CAS Sample ID #: EJ1889-S2
Metaldehyde Equivalents Recovered: 131%
GC run # 37243, set MV-1, dated 11/17/91

* Expressed as metaldehyde equivalents

FIGURE 8

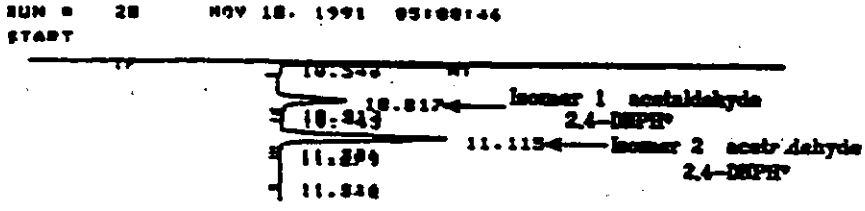
Typical Chromatogram

Soil Control + 1.0 ppm Metaldehyde

(0-6")

High Fortification

Attenuation = 2'



EN-CAS Sample ID #: EJ1889-S5
Metaldehyde Equivalents Recovered: 95%
GC run # 37243, set MV-1, dated 11/18/91

* Expressed as metaldehyde equivalents

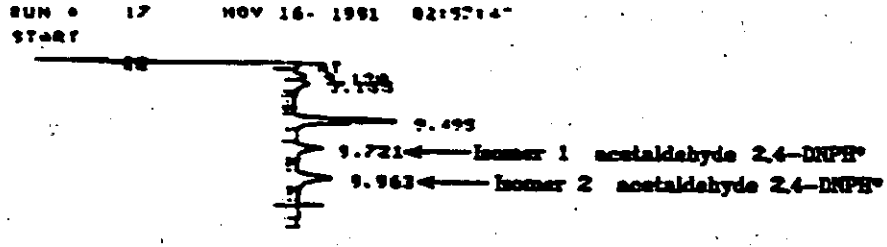
FIGURE 9

Typical Chromatogram

Soil Control

(6-12")

Attenuation = 2^4



EN-CAS Sample ID #: EJ1890-C2
Metaldehyde Equivalents Found: <0.02 ppm
GC Run # 37237, set MV2, dated 11/16/91

* Expressed as metaldehyde equivalents

FIGURE 10

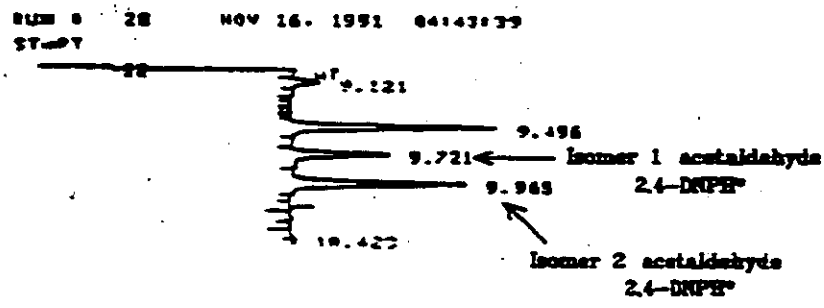
Typical Chromatogram

Soil Control + 0.02 ppm Metaldehyde

(6-12")

Low Fortification

Attenuation = 2^4



EN-CAS Sample ID #: E71890-S2
Metaldehyde Equivalents Recovered: 109%
GC run # 37237, set MV2, dated 11/16/91

* Expressed as metaldehyde equivalents

FIGURE 11

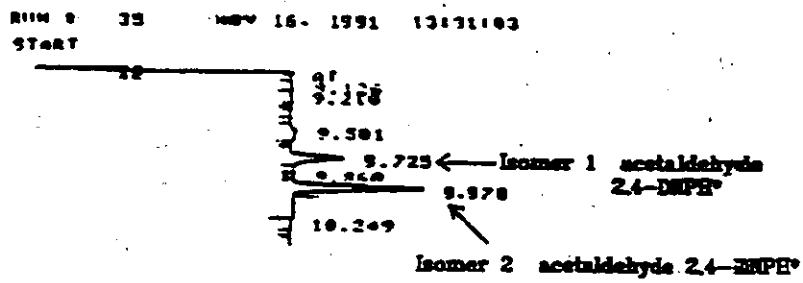
Typical Chromatogram

Soil Control + 1.0 ppm Metaldehyde

(6-12")

High Fortification

Attenuation = 2'



EN-CAS Sample ID #: EJ1890-S5
Metaldehyde Equivalents Recovered: 117%
GC run # 37237, set MV2, dated 11/16/91

* Expressed as metaldehyde equivalents

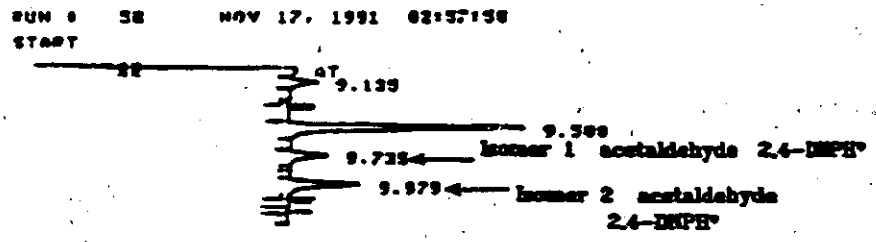
FIGURE 12

Typical Chromatogram

Soil Control

(12-18")

Attenuation = 2^4



EN-CAS Sample ID #: EJ1891-C1
Metaldehyde Equivalents Found: <0.02 ppm (0.0071 ppm)
GC run # 37239, set MV3, dated 11/17/91

* Expressed as metaldehyde equivalents

FIGURE 13

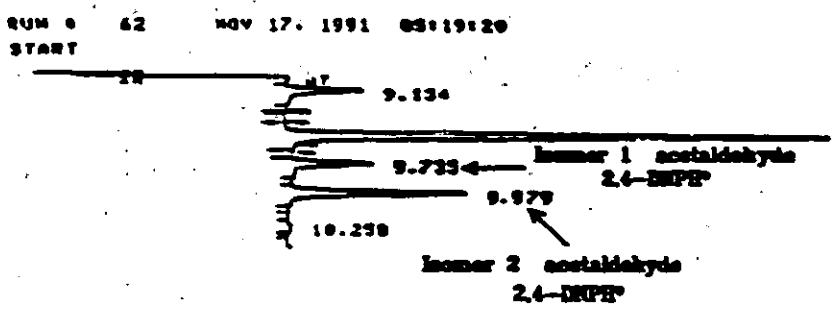
Typical Chromatogram

Soil Control + 0.02 ppm Metaldehyde

(12-18°)

Low Fortification

Attenuation = 2^4



EN-CAS Sample ID #: EJ1891-S2
Metaldehyde Equivalents Recovered: 91%
GC run # 37239, set MV3, dated 11/17/91

* Expressed as metaldehyde equivalents

FIGURE 14

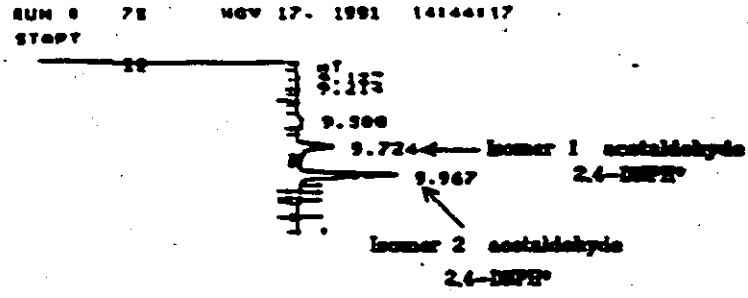
Typical Chromatogram

Soil Control + 1.0 ppm Metaldehyde

(12-18")

High Fortification

Attenuation = 2'

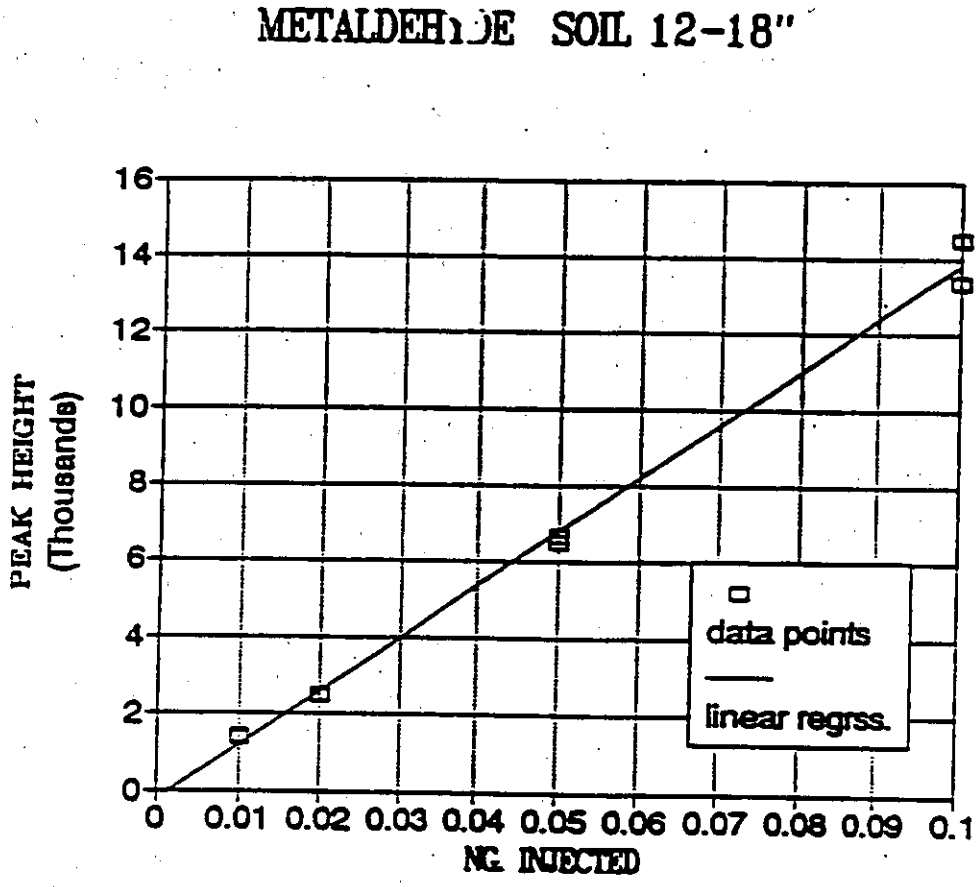


EN-CAS Sample ID #: EJ1891-S6
Metaldehyde Equivalents Recovered: 94%
GC run # 37239, set MV3, dated 11/17/91

* Expressed as metaldehyde equivalents

FIGURE 15

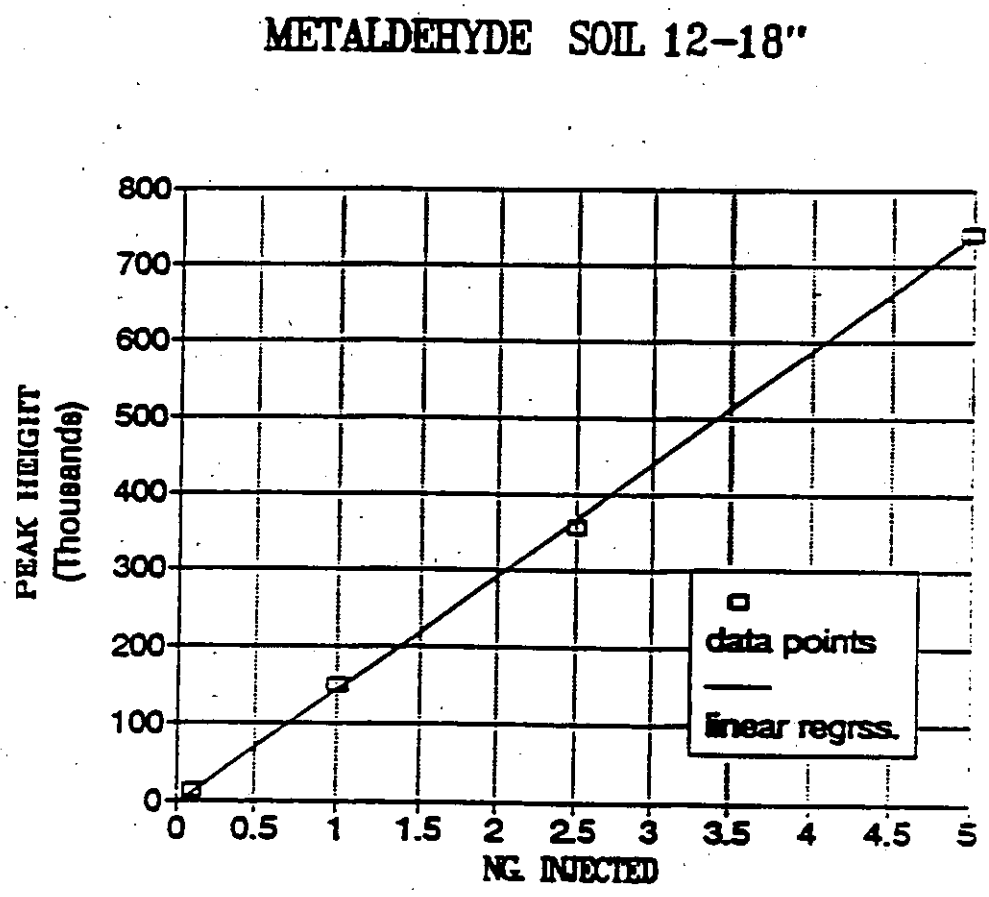
Typical GC Calibration Curve for 0.01 - 0.10 ng



GC run # 37239, set MV3, dated 11/18/91

FIGURE 16

Typical GC Calibration Curve for 0.10 - 5 ng



GC run # 37239, set MV3, dated 11/18/91