Determination of 1,3-Dimethylurea in Soil by Gas Chromatography

I. SUMMARY/INTRODUCTION

This method is intended for determining residues of 1,3-dimethylurea (DMU) in soil. It has been validated for soil concentrations of DMU between 0.02 to 1.0 ppm.

Metam-sodium (sodium salt of methyl carbamothioic acid, CAS Registry No. 137-42-8) is the active ingredient in the soil fumigant marketed under the tradename "Vapam". 1,3-Dimethylurea (CAS Registry No. 96-31-1) is a compound that has been identified to be present in a soil-metabolism study (reference 1). Chemical structures are given below.

$CH_3-NH-C(=S)-S^-Na^+$	$(CH_3-NH)_2C=O$
metam-sodium	1,3-dimethylurea (DMU)
FW: 129.17	FW: 88.11

In the field, 100-g samples of soil are placed in glass jars. Water is added to the soil samples, the jars are each capped with a Teflon-lined lid, and the capped jars are immediately placed in a freezer. In the laboratory, DMU is extracted directly from the soil by shaking the thawed sample of soil with methanol and water. The sample is centrifuged to obtain distinct soil and water phases. If particulate material remains suspended in the aqueous extract, the extract must be filtered. An aliquot of the clear aqueous extract is removed, and the water is evaporated. The residue is dissolved in methanol, and the DMU is quantified by using gas chromatography with nitrogen detection.

II. MATERIALS/METHODS

The equipment and reagents described below were used to generate the data and chromatograms presented in this report. Equipment with equivalent performance specifications and reagents of comparable purity can be used.

A. Apparatus

1. Gas Chromatograph. Varian model 2100 used with manual injections.

2. Coulson Electrolytic Conductivity Detector. Operated in the nitrogen detection-mode.

3. Gas-Chromatographic Column. 15 m by 0.53 mm i.d. capillary column with a 1.0-um film thickness of polyethylene glycol (DB-WAX, J & W Scientific, catalog no. 125-7012). A 60-cm (2-ft) by 0.53 mm i.d., phenyl-methyl siloxane deactivated, uncoated, fused silica guard column (Restek Corporation, catalog no. 10045) was also used.

4. Shaker. Reciprocating movement (Eberbach Corporation, Ann Arbor, MI).

5. Centrifuge. (1) Equipped to accept 8-oz bottles and capable of attaining 2000 - 3000 rpm (IEC HN-SII; Damon/ International Equipment Company, Needham Heights, MA). (2) Equipped to accept 50-mL centrifuge tubes and capable of attaining 2000 - 3000 rpm (IEC Clinical Centrifuge; Damon/International Equipment Company).

6. Glass Centrifuge Bottles. 8-oz, widemouthed bottles.

7. Centrifuge Tubes. 50-mL capacity with screwcap lids.

8. Syringes. 10-uL capacity, 26-gauge needle (Hamilton 701N) for injections into gas chromatograph.

9. Filter. 0.45-um Millipore filter.

10. Millipore Filtering Apparatus.

11. Test Tubes. 5- to 7-mL in capacity.

12. Flasks. 500-mL capacity, round-bottom.

B. Reagents

1. Solvents. Methanol and water. All solvents must be of high purity and suitable for use in trace organic analyses by gas chromatography.

2. 1,3-Dimethylurea. 99% Purity, available from Aldrich Chemical Co., Inc. (catalog no. D19,045-4) and Chem Service, Inc. (catalog no. 0-986; P. O. Box 3108, West Chester, PA 19381).

3. Silanization Reagent. Dimethyldichlorosilane for silane-treating round-bottom flasks and test tubes (Supelco, catalog no. 3-3009). Prepare a 5% solution in hexane.

4. Calibration and Fortification Solutions.

To prepare a 1.00 mg/mL (= 1000 ug/mL) stock solution of an analyte, place a known quantity (± 0.1 mg) of

50 or 100 mg of primary standard of known purity into a 50- or 100-mL volumetric flask, as appropriate.

The weight of primary standard used should take into account the purity of the primary standard.

Add some solvent (methanol or water) to the volumetric flask to initially dissolve the analyte. Then, fill the flask with solvent to the volumetric mark. Close the flask with a Teflon or ground-glass cap, and mix thoroughly. Use methanol for preparing subsequent dilutions of both the DMU calibration and fortification solutions.

To prepare working calibration solutions, serially dilute the stock calibration solution by volume with methanol to give 4.0, 2.0, 0.80, and 0.40 ug/mL solutions or other concentrations as required. Dilute the stock fortification solution by volume with methanol to give a 100, 10, and 1.0 ug/mL solutions, or other concentrations as required.

C. Analytical Procedure

1. Extraction

Add 50 mL of methanol to the sample consisting of 100-g of soil and 50 mL of water in an 8-oz bottle. Allow the sample to thaw. Shake the sample on a reciprocating shaker for 1 hr. Centrifuge the sample for about 10 to 15 min at about 2000 to 3000 rpm to obtain distinct soil and liquid phases. If suspended material cannot be completely settled, filter the aqueous extract through a 0.45-um filter. Place a 20.0-mL aliquot of the clear extract in a 500-mL silanized round-bottom flask. Remove the methanol and water under reduced pressure by using an evaporator with a heated water bath at about 45° to 50°C. Add 3.0 mL of methanol to the residual material in the flask. Transfer the methanol extract to a silanized test tube. Rinse the flask with 1 mL of methanol, and transfer the methanol to the test tube. Use a steam bath to obtain a final volume of 1.0 mL for analysis using gas chromatography.

2. Fortification

Analyze unfortified and fortified control samples with each sample set to demonstrate method recovery. For example, for 100-g samples, place 100 g of untreated control soil into an 8-oz widemouthed bottle, and add the appropriate volume of the fortification solutions to produce a fortification levels of 0.02, 0.10, or 1.00 ppm, or other

appropriate levels to match the levels found in the field samples. Add 50 mL of water and 50 mL of methanol to the soil sample. Extract the sample as detailed in section C.1 above.

D. Instrumentation

1. Operating Conditions

Follow the manufacturer's instructions for operation of the gas chromatograph and Coulson electrolytic conductivity detector. The specific conditions listed below were used to generate the data and chromatograms presented in this report.

Gas Chromatograph:

Carrier gas:	hydrogen.
Inlet type:	0.25-inch quartz liner (catalog no. 210-1064, J & W Scientific), direct injection
Inlet temperature:	240°C
Oven temperature:	155°C (isothermal)
Volume injected:	3.0 uL

Coulson Electolytic Conductivity Detector:

Pyrolysis temperature:	810°C
Pyrolysis gas:	hydrogen
Catalyst:	nickel

Quantitation: Peak height; external standard

Using the above conditions the elution times of DMU was 2.5 min. See Figures 1 and 3 for typical chromatograms.

2. Calibration

Calibrate the gas chromatograph by using the analyte calibration solutions specified in section II.B.4. Calibrate the instrument by using the 4.0, 2.0, 0.80, and 0.40 ug/mL solutions.

3. Analysis of Extracts

Inject the sample extracts using the same conditions used for calibration. The identity of the analyte peak in the sample chromatogram is assigned based upon the coincidence of retention times with those of the calibration chromatograms. If the response of a peak identified as an analyte exceeds that of the highest injected calibration solution, dilute the sample extract until its response is within the

calibrated range. Reinject the calibration solution after injection of every two to four sample extracts and at the end of the chromatographic run. Calculate the concentration of the analyte in the sample extract by comparing it to the closest standard (peak height), by use of a standard curve, or other accepted quantitation techniques.

E. Interferences

Extractives from soil could potentially contribute peaks with a retention time coincident with or near that of the analyte. Satisfactory resolution can usually be achieved with appropriate oven temperature manipulations or column selection (length, phase). Figures 1 and 3 show typical chromatograms. Analyze extracts of samples from untreated plots to demonstrate the absence of interferences from sample matrices, solvents, and labware. The resolution provided by capillary columns combined with the selectivity afforded by the Coulson electrolytic conductivity detector operated in the nitrogen mode should minimize any problems of misidentification.

F. Confirmatory Techniques

Unexpected positive results, as in untreated control or pre-application samples, should be confirmed by other means. Confirmation can be achieved by quantitation by using a different detector type, such as a mass-selective detector. Confirmation can also be achieved by using a different column, e.g., Pennwalt 223/KOH.

G. Calculations

The concentration of the analyte in the original sample is calculated by using the external standard method, i.e., the response obtained for the analyte in the sample extract is compared to the response obtained from a separate injection of a known amount of analyte (calibration solution). It is assumed for the calculations outlined below that the injection volumes for all calibration solutions and sample extracts are fixed at the same volume.

1. Linear Detector-Response

A single-concentration standard is repeatedly injected throughout the analytical run interspersed with the sample extracts. The amount injected is recorded in nanograms; the detector response is measured as a peak height in millimeters. All detector responses from injection of the standard must be within 10% of the mean of all the responses for the standard throughout the run.

An average sensitivity factor, S, in mm/ng is calculated based on the mean response and amount injected.

The peak-height response (mm) from injection of the sample extract is recorded. This value is divided by the sensitivity factor (mm/ng) to obtained the ng of analyte found in the sample injection. This value is divided by the amount (mg) of soil represented by the injection of the extract [uL injected x (mg of soil extractives/uL of extract)]. The result is ng/mg (= ug/g) or ppm of analyte found. See Figure 2 for an example.

C. Dry-Weight Basis

This method determines the residues on an as-received basis. If it is desired to express the residue values on a dry-weight basis, compensation is necessary for water present in the sample. Percent moisture can be determined by drying a subsample at 130 C for 3 hr.

$$\text{ppm, dry wt.} = \text{ppm, wet wt.} \times \frac{\text{wet weight}}{\text{dry weight}}$$