Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Glyphosate

MRID #: 443265-07

Matrix: Water

Analysis: GC/FPD

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1 **SUMMARY/INTRODUCTION**

This method is intended for determining residues of the trimethylsulfonium cation (TMS) in soil at levels from 0.05 to 5 ppm and in water at levels from 0.01 to 0.1 ppm. Glyphosate-trimesium, which is composed of a 1:1 mixture of the trimethylsulfonium cation [CAS Registry No. 676-84-6] and the glyphosate(1-) anion, is the active herbicidal ingredient in the formulated product marketed by Zeneca Ag Products under the trademark, TOUCHDOWN®.

The TMS is extracted from water by passage through a column packed with cation exchange resin. The TMS is eluted from the column with concentrated potassium chloride (KCl) solution.

The TMS is extracted from soil samples by shaking with 10% aqueous potassium hydroxide solution. An aliquot of the aqueous soil extract is cleaned-up. This is accomplished by acidifying the extract, adding activated charcoal, and removing the charcoal by centrifugation followed by filtration.

The cleaned-up soil extract or column eluate for the water sample is heated at 100° C in the presence of tin(II) chloride, potassium hydroxide, and toluene to dealkylate the TMS to dimethylsulfide (DMS). The DMS, which is trapped in the toluene, is quantitated by using capillary, gas chromatography and a sulfur chemiluminescence detector (SCD) or a flame photometric detector (FPD).

Recoveries of TMS from sandy loam soil fortified at 0.05, 0.5, and 5.0 mg/kg ranged from 94 to 113%, with a mean recovery of 100% (n= 9) and coefficient of variation of 6.0%. Recoveries of TMS from commercial drinking water fortified at 0.01 and 0.10 mg/kg ranged from 97 to 112%,

with a mean recovery of 105% (n= 6) and coefficient of variation of 6.6%.

2 MATERIAL/METHODS

The recommended equipment and reagents are described. Equipment with equivalent performance specifications and reagents of comparable purity can be substituted.

2.1 Apparatus

2.1.1 4-oz Wide-Mouthed Jars. Jars with screw-caps.

2.1.2 Shaker. Eberbach Corporation, Ann Arbor, MI.

2.1.3 Centrifuge. An International Equipment Company Centra-8 centrifuge (Needham Heights, MA).

2.1.4 Capsule Vials. 28 x 70 mm, 24-mL (6 drams) vials with screw-caps (Kimble, catalog no. 60957C-6).

2.1.5 10-cc Syringes. Disposable, plastic syringes with Luer-Lok tips (Baxter; catalog no. S9521-10L)

2.1.6 Syringe Filters. Disposable, 25-mm diameter, 0.45-um pore-size with Luer hub (Nylon Acrodisc; Gelman Sciences, Ann Arbor, MI; catalog no. 4438).

2.1.7 Column Rack. Econo System Rack (Bio-Rad, Hercules, CA; catalog no. 731-8200).

2.1.8 Columns. 20 by 1.0 cm i.d. chromatographic columns (Bio-Rad, catalog no. 737-1021).

2.1.9 Beakers. 100-mL capacity, borosilicate glass beakers.

2.1.10 Pipets and Pipet Filler. Disposable, 2- and 10-mL capacity. Red pipet filler (Baxter Scientific Products, catalog no. P5311-1).

2.1.11 Graduated Cylinders. 10-, 25-, 50-, 100-, and 1000-mL capacity.

2.1.12 15-mL Glass Vials with Screw-Caps. Each cap has a hole and contains a silicone septum lined with a perfluoroethylene polymer (Supelco, Bellefonte, PA; catalog no. 2-3284).

2.1.13 Electric Heating-Module. A Multi-Blok Heater (115 V, 50/60 Hz, 100 watts) made by Lab-Line Instruments, Inc. (Melrose Park, IL). The unit is equipped with an aluminum heating block (Supelco; catalog no. 3-3316) drilled with 8 holes (21 mm wide, 31 mm deep) to accept glass vials for heating.

2.1.14 Disposable Pipets. 15-cm length, flint-glass Pasteur pipets

2.1.15 Autosampler Vials with Inserts. 2-mL crimp-top vials (Sunbrokers, catalog no. 200-000) with crimp-tops (Sunbrokers, catalog no. 200-100) and 200-uL, flat bottom, limited-volume inserts (Sunbrokers, catalog no. 200-232)

2.1.16 Gas-Chromatographic System. A Hewlett-Packard (HP) model 5880A, Level 4, gas chromatograph equipped with a HP model 7673A autosampler/injector. The autosampler/injector is equipped with a 10-uL syringe with a 23-gauge needle (Hamilton 701N). The instrument is equipped with a 350B Sulfur Chemiluminescence Detector made by Sievers (Boulder, CO) and an HP 3394A Integrator.

Alternatively, an HP model 5890 gas chromatograph equipped with an HP model 7673A high speed autosampler/injector. The autosampler is equipped with a 10-uL syringe with a 23-gauge needle (Hamilton 701N). The instrument is equipped with a

flame photometric detector with a sulfur bandpass filter and an HP 3396A integrator.

2.1.17 Gas-Chromatographic Column. A 30 m by 0.53 mm i.d., fused-silica, capillary column bonded with a 1.5-um thickness of (95%)-dimethyl-(5%)-diphenylsiloxane, Durabond-5 (catalog no. 125-5032; J&W Scientific; Folsom, CA).

2.2 Reagents and Materials

2.2.1 Potassium Hydroxide. Dry solid pellets with a minimum assay of 85% (EM Science, catalog no. PX 1490-1).

2.2.2 10% Potassium Hydroxide Solution. Dissolve 100 g per liter of high-purity water.

2.2.3 Concentrated Hydrochloric Acid. 36.5-38% 'Baker Analyzed' reagent (J. T. Baker, Phillipsburg, NJ).

2.2.4 Activated Carbon. Darco® G-60 -100 mesh, powder (Aldrich Chemical Co., catalog no. 24,227-6).

2.2.5 Toluene. A high-purity grade of solvent suitable for trace-organic analyses.

2.2.6 Water. High-purity water suitable for trace organic analysis.

2.2.7 1.0 N Hydrochloric Acid (HCl). Aqueous solution; available from Mallincrodt (catalog no. 6388). Note: Dilution of 83 mL of concentrated reagent HCl to 1.0 liter will yield a 1 N HCl solution.

2.2.8 0.1 N HCl Solution. 0.1 HCl is used for preparation of TMS solutions. To prepare a 0.1 N HCl solution, dilute the 1.0 N HCl 1:10.

2.2.9 Cation-Exchange Resin for Concentration. AG 50W-X2, 100-200 mesh, hydrogen form, analytical-grade cation exchange resin (Bio-Rad Labs.; cat. # 142-1241).

2.2.10 Solid Glass Balls. 1.5- to 2-mm diameter glass balls (Jencons Ltd.; marketed by Scientific Products (Baxter) catalog no. G6031-15).

2.2.11 Potassium Chloride. 99+ % purity (Aldrich, catalog no. 20,800-0).

2.2.12 1 M Potassium Chloride Solution. 74.56 g/L of water.

2.2.13 Tin(II) Chloride Dihydrate ($SnCl_2 \cdot 2H_2O$). Assay $\geq$ 98% (EM Science, catalog no. SX0885-1).

2.3 Reference Materials

2.3.1 Reference Standard. Trimethylsulfonium iodide, assay $\geq$ 99%, is available from Zeneca Ag Products, 1200 South 47th Street, Box Number 4023, Richmond, CA 94804-0023; Attention: Manager, Environmental Sciences Department.

The Material Identification number of the TMS iodide used in this study was ASW 1441A (Request number was 1993-I156).

2.3.2 Calibration and Fortification Stock Solutions. Prepare two separate stock solutions. Calibration solutions are used to calibrate the instrument. Fortification solutions are used to fortify samples in order to demonstrate procedural recoveries. All solutions are prepared with 0.1 N HCl solution to inhibit microbial growth.

Prepare a stock solution containing 2.66 mg of trimethylsulfonium iodide per milliliter of 0.1 N HCl. [The formula weights of TMS, iodide, and TMS iodide are 77, 127, 77.18, 126.90,

and 204, respectively; therefore the TMS/TMS iodide ratio is 0.377, and 2.66 mg TMS iodide/mL multiplied times 0.377 equals 1.00 mg TMS/mL].

To prepare each stock solution place a known quantity (± 0.1 mg), e.g., 266 mg, of TMS iodide in a 4-oz amber, glass bottle. Multiply the amount of milligrams weighed out by 0.377 to calculate the weight of 0.1 N HCl to add to the TMS iodide, e.g., if exactly 266 mg are weighed out, add 100 g of 0.1 N HCl. Add the calculated weight of 0.1 N HCl to the 4-oz bottle. Close the bottle with a Poly-Seal cap or a cap lined with a fluorocarbon polymer, such as Teflon®. Mix the contents thoroughly to dissolve the TMS iodide. The concentration of the stock solution is 1.0 mg or 1000 ug TMS/mL. Starting with the stock solution, make 1:10 serial dilutions to prepare 100, 10 and 1.0 ug TMS/mL solutions. Use 0.1 N HCl to prepare all solutions.

3 ANALYTICAL PROCEDURE

3.1 Extraction of Soil.

3.1.1 Place 25 g of soil and 50 mL of 10% KOH solution in a 4-oz jar.

Note: 1) The instruction assumes that the moisture content of the soil sample is ≤ 20% by weight and that the resulting TMS analytical error of ≤ 10% is acceptable. If more accuracy is required, moisture determination of the soil sample is required prior to extraction; decrease the amount of KOH solution added by the amount of water contained in the soil sample. 2) A PTFE-liner for the cap is unnecessary. Do not use aluminum foil as it will react with the KOH. 3) Avoid personal contact with the KOH solution. Flush any contacted area with plenty of water.

3.1.2 Securely cap the jar, and shake for 1 hr on a mechanical shaker.

3.1.3 Centrifuge the jar, e.g., 2500 rpm for 15 min, to settle the soil.

3.1.4 Decant the supernatant KOH extract into a clean 4-oz jar. The extract represents 25 g/50 mL or 0.5 g of soil per milliliter.

Note: It is not necessary to decant the supernate; the required aliquot can be removed directly from the jar with a pipet.

3.1.5 To continue soil analysis, skip to section 3.3.

3.2 Extraction of Water

The use of a column, as described below to concentrate the TMS in water samples, is necessary only if a 0.01-ppm detection limit is desired, and the detector sensitivity for instrumental analysis is inadequate. Direct dealkylation of 10 mL of water sample in the presence of 0.5 mL of toluene would allow quantitation at an LOQ of 0.01 ppm under optimum conditions; see section 3.4. If residues >0.02 ppm are expected, direct dealkylation of the water samples is recommended.

3.2.1 Prepare Column: Use a 20 by 1.0-cm (i.d.) Bio-Rad chromatographic column. Place 2.5 g of AG® 50W-X2 resin in a 100-mL beaker and add about 15 mL of pure water. Pour the resin-water slurry into the column. After the water has drained from the column, wash the column with about 15 mL of pure water using roughly 5-mL portions. After the last wash water has been added and most of the resin has settled, but before the last of the water has entered the resin bed, place about 2 g of glass balls on top of the resin.

Note: 1) Water, in addition to that specified above, can be used for resin transfer, column washing, etc. 2) The column can be prepared several days in advance. It is only necessary that the bottom end of the column is capped, and the resin bed is kept filled with water.

3.2.2 Add 25 mL of the water sample portionwise to the column.

3.2.3 Elute the column with 7 mL of 1 M KCl solution. Collect the eluate directly in a 15-mL dealkylation vial.

3.2.4 To continue water analysis, skip to section 3.4

3.3 Cleanup of Soil Extract

3.3.1 Place a 14-mL aliquot of the soil extract in a 6-dram vial.

3.3.2 Add 2 mL of concentrated HCl and 250-260 mg of activated carbon to the vial. Shake the mixture, and allow it to stand for 10 to 15 min to let the carbon settle.

Note: Activated carbon also removes small amounts of TMS from solution. Decreasing the amount of carbon used will result in less loss of TMS but will also result in more background.

3.3.3 Centrifuge the vials, e.g., 2500 rpm for 15 min.

3.3.4 Carefully draw the supernate into the barrel of a 10-cc syringe. Fit a 0.45-um filter to the syringe barrel. Filter the liquid into a clean 6-dram vial. The extract now represents 7 g/16 mL or 0.44 g of soil per milliliter.

Note: Some soils, especially silty clay loams, are difficult to filter and can require the use of as many as four filters.

3.3.5 To continue soil analysis, proceed to section 3.4

3.4 Dealkylation

3.4.1 Place 5.0 mL of a 1.0 ug TMS/mL calibration solution in a 15-mL dealkylation vial for use as a standard.

3.4.2 Soil. Place 8.0 mL of the cleaned soil extract from section 3.3.4 into a 15-mL vial. This volume represents 3.5 grams of soil.

Water. Use the column eluate, 7 mL, from section 3.2.3, or place 10 mL of water into a 15-mL vial.

Note: The above suggested volumes are for samples that contain TMS residues at the LOQ. If high residues are anticipated, use less soil extract or less water sample. The dealkylation vial should contain a minimum of 5 mL of water. If, for example, only one milliliter of extract or water sample is used, then add 4 mL of distilled water to the vial.

3.4.3 Add 200 to 250 mg of tin(II) chloride dihydrate to each 15-mL vial, and swirl the vial gently to partially suspend the tin(II) chloride. Add 0.5 mL of toluene to vials containing the soil extract. Add 1 mL of toluene to the column eluate of the water sample. Add 0.5 mL toluene to 10 mL of water for direct dealkylation. Add 5.0 mL of toluene to the vial containing the calibration solution.

Note: 1) The recommended amounts of toluene added is based on samples containing residues at or below the LOQ. If high residues are anticipated, the amount of water sample or soil extract used should be decreased, or the water sample or soil extract should be diluted with pure water. The amount of toluene can be increased, but the total volume

constraints of the vial must be kept in mind. Use of only 0.5 mL of toluene means that accurate volumetric removal of the toluene for dilution purposes prior to analysis will be extremely difficult to accomplish. 2) The tin(II) chloride is added as an antioxidant to minimize oxidation of the DMS to dimethylsulfoxide.

3.4.4 Add to the vial, 5 - 5.5 g of KOH pellets to water samples/eluates or 7 - 7.5 g of KOH pellets to soil extracts. Cap the vial immediately.

Note: The KOH pellets should be added smoothly, e.g., on a firm sheet of paper, to prevent loss of toluene through splashing. They should be added quickly because of the rapid generation of heat. Ensure that all pellets are of a size that will pass into the vial easily. There can be bottle to bottle variations in the pellet size. KOH pellets are hygroscopic.

3.4.5 Heat the vial at 100 °C for 1 to 2 hr in an electric heating module.

Note: 1) All vials should be heated for the same amount of time. 2) Occassionally, the septum in the cap could pop out; this is built into the procedure as a safety feature to relieve excessive pressure buildup due to unforseen circumstances, e.g., elevated heating block temperatures. If this occurs, discard the sample and repeat with a new aliquot of sample extract. Do not loosen the cap because the volatile DMS could escape. Appearance can be deceiving in that the seal is generally maintained even when the cap is a bit off of center. The adequacy of the seal can be confirmed after heating by inspection of the indentation left on the septum by the rim of the glass vial.

3.4.6 Carefully remove the hot vials from the heating block. Cool the vials by placement in an ice water bath. Alternatively, 1) allow the vials and their contents to cool to ambient temperature by locating the vial in a high draft area of the fume hood or 2) chill the vials by placing them in a freezer.

Note: The DMS solution in toluene is stable at ambient temperature for at least two weeks if it is left in the dealkylation vial which is tightly capped.

3.4.7 Centrifuge the vial, e.g., 15 min at 2500 rpm.

3.4.8 Unscrew the cap from the vial, and place an aliquot of the toluene in an autosampler vial fitted with a limited-volume insert. Crimp seal the vial immediately.

Note: Avoid areas that use or store carbon disulfide, which is used as a solvent for many applications. Carbon disulfide has a retention time nearly coincident to that for DMS.

3.5 Fortifications

Analyze residue-free control samples and fortified, residue-free control samples whenever possible along with any sample analysis. It is recommended that one control sample and two fortified control samples be analyzed each time for every set consisting of ten samples or less. One of the fortified samples should be fortified at the method's lower limit of quantitation (LOQ) of 0.05 ppm (soil) or 0.01 ppm (water). To prepare a 0.05- or 0.01-ppm, fortified sample, add 125 uL of a 10 ug TMS/mL fortification solution to 25 g of soil or 250 uL of a 1 ug TMS/mL fortification solution to 25 mL of water. The second fortified sample should be fortified at twice the LOQ or at a level expected in the unknown sample.

4 INSTRUMENTAL ANALYSIS CONDITIONS

Follow the manufacturer's instructions for operation of the gas chromatograph, autosampler/injector, sulfur chemiluminescence detector (SCD), and flame photometric detector (FPD). The specific conditions listed below were used to generate the data and chromatograms presented in this report.

4.1 Operating Parameters Outline

4.1.1 For the SCD, use 115° C for the inlet and isothermal column temperatures. Use helium as the carrier gas; set the column flow rate to about 7 mL/min. Set the flow rates of air (e.g., 280 mL/min), hydrogen (e.g., 200 mL/min), and auxillary helium supplied to the detector to the values recommended by the detector manufacturer. Use a 3-uL injection volume with a splitless single-piece liner with ~2 mm i.d. straight bore. The retention time of DMS is about 1 min; a large toluene peak will appear after about 2 min.

4.1.2 For the FPD, the column flow was 6 mL/min of helium. A splitless single-piece liner with ~2 mm i.d. straight bore was used. The inlet and column temperatures were 150° and 100° C isothermal, respectively. The air and hydrogen flows to the detector were 94 and 64 mL/min, respectively. The volume injected was 2 uL. Due to quenching of the detector response by residual toluene, at least a 5-min run time between injections is recommended.

4.2 Calibration and Analysis

Calibrate the gas chromatograph by using the appropriate TMS calibration standard prepared in section 2.3 and dealkylated in section 3.4.

For soil analyses, dilute 200 and 500 uL of the 1 ug/mL dealkylated standard (high level), with 800 and 500 uL of toluene, respectively, to prepare the 0.20 ug/mL (low-level) and 0.5 ug/mL (intermediate-level) standards.

For water analyses, dilute 250 and 500 uL of the 1 ug/mL dealkylated standard (high-level), with 750 and 500 uL of toluene, respectively, to prepare the 0.25 ug/mL (low-level) and 0.5 ug/mL (intermediate-level) standards.

Even though the TMS has been dealkylated to DMS, it is simplest to continue expressing all concentrations in TMS equivalents. Depending on the overall precision of the chromatographic system, the analyst may opt to make duplicate injections of all calibration standards and sample extracts. The identity of the analyte peak in the sample chromatogram is assigned based upon the coincidence of retention times with the DMS peak of the calibrant chromatogram. Sample extracts containing residues that are higher than the 1 ug/mL calibrant solution must be diluted and reanalyzed.

Following is a suggested analytical scheme. Injections can be made in the following order:

1. Replicate injections (3 to 5) of the high-level standard to equilibrate the column.

2. Injections of the high-, intermediate-, and low-level standards to establish the calibration curve.

3. Injection of up to 7 samples. These samples can be extracts of untreated controls, fortified controls, treated-field samples, etc. Sample extracts containing residues that are higher than the high-level calibrant solution must be diluted and reanalyzed.

4. Injections of the high-, intermediate-, and low-level standards to establish the calibration curve.

5. Repeat steps 3 and 4 until all samples have been injected.

5 CALCULATIONS

The concentration of the analytes in the original sample is calculated by using the external standard method, that is, the response obtained for the analytes in the sample extract is compared to the response obtained for a separate injection(s) of a known amount of analyte in the calibration solution. To use the calculations shown below, the injection volumes for all calibration solutions and sample extracts must be fixed at the same volume. The average response obtained for all TMS standards used during the run is used for calculating the concentration of TMS in the samples.

5.1 Linear Response Calculation Methods

Appendix A gives sample calculations using both the calibration factor method described in 5.1.1 and the linear regression methods described in 5.1.2.

5.1.1 Calibration factor. Calculate the average response factor, F(avg), for injection of high-, intermediate- and low-level calibration solutions;

$$F(avg) = [F(high) + F(intermediate) + F(low)]/3$$

Individual-level response factors, F, are calculated as follows:

$$F = \frac{C}{R}$$

Where

F = response factor ((ug/mL)/cm)

C = concentration of calibration solution (μg/mL)

R = average response units from detector for calibration solution (cm)

Calculate the analyte in the sample as in 5.1.4.

5.1.2 Linear Regression Analysis. Alternatively, perform a linear regression analysis on the results of the injections of the calibration standards using TMS concentration (x-axis) versus the SCD detector response (y-axis). The regression analysis will provide the constants m and b for the linear equation, $y = mx + b$, where m is the slope and b is the y-intercept at $x = 0$. Calculate the TMS concentration, X, in each sample extract using the equation $x = (y - b)/m$. If any background corrections are applied, substract the responses. Calculate the analyte in the sample as in 5.2.2.

5.1.3 Matrix in final extract. Calculate the concentration of the sample matrix; that is, the amount of soil or water that the final extract represents, as follows:

For soil sample:

$$C = \frac{W\ (\text{sample})}{V\ (\text{solvent})} \times \frac{b \times V\ (\text{aliquot})}{V\ (\text{toluene})}$$

Where:

C = concentration of matrix (g/mL)

W (sample) = weight of soil extracted (g)

V (solvent) = volume of extracting solvent used (mL); volume includes the endogenous water in the soil (mL). [Analyses in this report have disregarded volume contribution from endogenous water as being nonsignificant, i.e., ≤ 10 %]

b = 0.875. Factor representing removal of 14 mL of KOH extract and diluting to 16 mL by addition of 2 mL of conc. HCl solution

V (aliquot) = volume of final cleaned aliquot placed in dealkylation vial (mL)

V (toluene) = volume of toluene used to trap the DMS; volume includes any toluene dilutions (mL)

For water sample:

$$C = \frac{W\ (sample)}{V\ (toluene)}$$

Where:

C = concentration of matrix (g/mL)

W (sample) = (1) weight of water sample placed directly in dealkylation vial; weight does not include any pure water used for diluting the sample (g), or (2) weight of water sample added to ion exchange column to concentrate the TMS (g)

V (toluene) = volume of toluene used to trap DMS (mL); volume includes any toluene dilutions (mL)

5.1.4 Analyte in sample. Calculate the analyte concentration, A, in the original sample as follows:

$$A = \frac{F \times R}{C}$$

Where

A = concentration of analyte in original sample (µg/g, mg/kg, or ppm)

F = response factor (µg/mL)/cm

R = average sample response from detector for sample (cm)

C = concentration of matrix in final extract (g/mL)

5.2 Nonlinear Response Calculation Methods

For detector responses that significantly deviate from linearity, such as the FPD, the following procedure can be used to calculate extract concentrations. Appendix A gives an example calculation for the linear regression analysis method described in 5.2.1

5.2.1 Calculation of analyte concentration in extract.

Perform a linear regression analysis on the results of the injections of the calibration standards using TMS concentration (x-axis) versus the square root of the FPD detector response (y-axis). The regression analysis will provide the constants m and b for the linear equation, $y = mx + b$, where m is the slope and b is the y-intercept at $x = 0$. Calculate the TMS concentration, X, in each sample extract using the equation $x = (y - b)/m$. Note that y is the square root of the detector response. If any background corrections are applied, subtract the square root of the responses, rather than the responses themselves.

Alternatively, the calibration data can be plotted on graph paper, and the TMS concentration, X, in each sample extract can be determined from the calibration curve. Calculate the analyte in the sample as in 5.2.2.

5.2.2 Calculation of analyte in sample.

Calculate the analyte concentration, A, in the original sample as follows:

A (µg/g, mg/kg, or ppm) = X/C

Where

X = analyte concentration in the final extract calculated from the curve fit equation or determined from a graphical standard curve (µg/mL)

C = matrix concentration in extract, from section 5.1.3 (g/mL).

6 INTERFERENCES

6.1 Carbon Disulfide

Because analytical laboratories sometimes stock and use large amounts of carbon disulfide, contamination by carbon disulfide is a potential problem. Contaminations have occurred from 1) using toluene from a bottle stored in a cabinet containing a bottle of carbon disulfide and 2) using a centrifuge immediately after someone else had used it to centrifuge bottles containing carbon disulfide as the extraction solvent. Carbon disulfide does resolve chromatographically from DMS if both are at low concentrations.

6.2 Dimethylsulfide (DMS)

TMS is not the only source of DMS in the final solution subjected to dealkylation. S-Methylmethionine, called Vitamin U in the Merck Index, is believed to be at least one source of DMS in samples. Under alkaline conditions, Vitamin U can readily produce DMS. It has been isolated from cabbage and subsequently detected in the foliage of a range of higher plants, including parsley, pepper, onion, lettuce, and turnip. Its presence has been established in tomato foliage and fruit, potato, and green tea. Cabbage leaves and kohlrabi were found to contain relatively high levels of the compound, corresponding to as much as 0.2 and 0.1% of the tissue dry weight, respectively. Vitamin U is probably ubiquitous in all plant tissues (reference 1). Plant tissue exist in soil samples as root hairs and detritus and can contribute background DMS to soil samples.

7 CONFIRMATORY TECHNIQUES

Unexpected positive results, as in untreated controls or preapplication samples, should generally be confirmed by other means. However, if analysis is conducted by a sulfur-selective detector and the retention time of the peak is coincident with that of DMS, the peak is probably due to DMS, so confirmatory work is not productive. The origin of the DMS is likely from endogenous precursors in the sample matrix. Because some peak resolution is lost in the SCD transfer line, the FPD is the better detector in terms of peak discrimination.

8 DISCUSSION

This method is a revised version of the soil and water portion of the method "*Determination of SC-0224 Cation Residues in Crops, Water, and Soil by Gas Chromatography*," (reference 2). Cleanup procedures have been expanded to lower background DMS originating from endogenous coextractives, and thus give lower "apparent" TMS residues. A column technique is used to concentrate the TMS in water prior to dealkylation. A capillary column is used for the gas chromatography. The choice of detectors on the chromatograph has been expanded to include both a flame photometric detector (FPD) and a sulfur chemiluminescence detector (SCD). The SCD has been added because the FPD responds nonlinearly to sulfur and requires more complex data handling than the linearly responding SCD.

8.1 Scope

This method is suitable for the determination of TMS in soil and water. Recovery data given in Table I reflect the methodology described herein.

8.2 Precision and Accuracy

Fortified soil and water samples were prepared as described under section 3.5, and analyzed according to this method to establish recoveries. Recoveries of TMS from sandy loam soil fortified at 0.05, 0.5, and 5.0 mg/kg ranged from 94 to 113%, with a mean recovery of 100% (n= 9) and coefficient of variation of 6.0%. Recoveries of TMS from commercial drinking water fortified at 0.01 and 0.10 mg/kg ranged from 97 to 112%, with a mean recovery of 105% (n= 6) and coefficient of variation of 6.6%. Table I lists the individual recoveries obtained from soil and water. Table II gives the soil characteristics. Emphasis is placed on sandy loam soil in this report as it is the soil most likely to be tested for residues when leaching potential is being investigated. Experience has shown that recovery from sandy loam soil is always >70%, but may be 50-70% for other soils, especially silt loams, due to strong binding of the TMS cation to the soils.

The precision of the method depends on variations in extraction, cleanup, dealkylation, and instrumental analysis. These variations can be evaluated from the data obtained during analysis of fortified samples. The coefficient of variations given in Table I are a measure of precision.

8.3 Detection Limit

The detection limit for a specific analyte in a specific matrix is based on the minimum detectability of the analyte, and the matrix concentration in the extract. The minimum detectable amount has been established as a response large enough that a 25% change can be distinguished. Also required is a signal-to-noise ratio of at least 10. The detection limit for a specific matrix is obtained by

dividing the minimum detectable amount by the amount of crop represented by the extract. Because the detection limit depends on the amount of sample cleaned up, the amount of time and effort expended on removing interfering coextractives, level of instrumental performance, etc., no effort was made to establish detection limits for the various matrices.

8.4 Lower Limit of Quantitation

The lower limit of quantitation (LOQ) is defined as the lowest concentration at which a method has been verified. It may differ from the detection limit. Due to the variability in instrumental performance, this value may exhibit some interlaboratory variation. LOQ values of 0.05 mg TMS/kg for soil and 0.01 mg TMS/kg for water were obtained from work conducted for this report (see Table I).

8.5 Matrix Effects

The absence of chromatographic matrix effects, that is, excessively enhanced recoveries, was verified by the analysis of a sandy loam soil extract fortified just prior to dealkylation. The result is listed in Table I.

8.6 Extract Analysis

Analyses were performed using a sulfur chemiluminescence detector (SCD) due to its highly selective and linear response to sulfur. Sample SCD chromatograms are given in Figures 1 and 2 for the analyses performed for this study. A sample SCD standard curve is given in Figure 4. Sample calculations are given in Appendix A. Because the SCD is not widely used in residue analysis, the traditional flame photometric detector (FPD) can also be used. Sample FPD chromatograms, corresponding to Figure 1 is given in Figure

3. A sample FPD standard curve is given in Figure 5. A sample calculation is given in Appendix A.

8.7 Dry-Weight Basis

This method determines the soil residues of TMS on an as-received basis. If it is desired to express the values on a dry-weight basis, compensation is necessary for water present in the sample.

8.8 Extraction Efficiency

The 10% KOH extraction of soil represents the harshest usable conditions for extracting the soil without decomposing the TMS.

8.9 Safety Precautions

Personnel untrained in the routine safe handling of chemicals and good laboratory practices must not attempt to use this procedure. Information on any specific chemical regarding physical properties, hazards, toxicity, and first-aid procedures can be found on the Material Safety Data Sheet (MSDS) accompanying the chemical or available from the supplier. In general, always wear safety glasses with side shields, work in a well ventilated area, avoid inhaling vapors, and avoid contact of the chemicals with skin and clothing. Flammable solvents should always be kept away from potential sources of ignition.

9 CONCLUSION

This method is selective for the analysis of TMS residues in soil and water. Only commercially available laboratory equipment and reagents are required. The analysis can be

completed by one person in an 8-hr period if an adequately homogenized sample is available. If possible, untreated and fortified samples should be extracted and analyzed with each set of samples to demonstrate absence of interferences and adequate recovery. If determination of TMS residues at a concentration other than the LOQ and ten times the LOQ is required, suitably fortified samples must be analyzed to validate this method at that concentration.

10 TABLES AND FIGURES

Table I.	Recoveries of TMS from Soil and Water
Table II.	Soil Characteristics
Figure 1.	Sample SCD chromatograms of an Iowa clay loam soil fortified at the LOQ of 0.05 mg/kg
Figure 2.	Sample SCD chromatograms of drinking water fortified at the LOQ of 0.01 mg/kg
Figure 3.	Sample FPD chromatograms of a Iowa clay loam soil fortified at the LOQ of 0.05 mg/kg
Figure 4.	Sample SCD calibration curve for DMS, as TMS equivalents, based on injections of 1.0-, 0.50-, and 0.20-ug/mL toluene solutions
Figure 5.	Sample FPD calibration curve for DMS, as TMS equivalents, based on injections of 1.0-, 0.75-, 0.50-, and 0.20-ug/mL toluene solutions