MANEB 3601
Hand Wash

$C_4H_6N_2S_4Mn$ MW: 265.2 CAS: 124-38-2 RTECS: OP07000

METHOD: 3601, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA : not applicable
NIOSH: not applicable
ACGIH: not applicable

PROPERTIES: powder, yellow, wettable; sparingly soluble in water and organic solvents; vp not significant

NAMES & SYNONYMS: manganous ethylenebis(dithiocarbamic acid), Manzate; Dithane M-22

SAMPLING

SAMPLER: PLASTIC BAG containing hand-wash solution,150 mL

SHIPMENT: add 1 g L-cysteine, 3 g $Na_4EDTA•H_2O$ to each sample, ship in refrigerant packs, 4 °C, via overnight express

SAMPLE STABILITY: at least 1 week at 4 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, UV detection

ANALYTE: ethylenebisdithiocarbamate anion

INJECTION VOLUME: 100 µL

MOBILE PHASE: 0.0675 M phosphate, 0.0525 M $NaClO_4$, pH 6.9, 1 g/L $Na_2EDTA•2H_2O$, 2 mL/min

COLUMN: Dionex AS7 anion exchange column, GS7 guard column or equivalent

DETECTOR: UV, 285 nm (λ max) or 254 nm

CALIBRATION: solutions of Maneb in 1% L-cysteine, 3% Na_2EDTA

RANGE: 0.03 to 15 mg/sample [1]

ESTIMATED LOD: 0.2 µg/mL or 0.03 mg/sample [1]

PRECISION ($\bar{S}_r$): 0.015 [1]

APPLICABILITY: This method determines Maneb washed from the hands of workers. It is applicable to the determination of Zineb, Mancozeb, and Nabam since these all convert to the same analyte when dissolved in EDTA solution.

INTERFERENCES: Not thoroughly investigated. No interferences have been found during method development.

OTHER METHODS: Maneb can also be determined by first methylating followed by HPLC analysis with a C18 column [2-5].

REAGENTS:

1. Maneb*, purity > 90%
2. Water, deionized
3. Mobile Phase, 0.0675 *M* phosphate buffer, 0.0525 *M* $NaClO_4$, 1 g/L $Na_2EDTA•2H_2O$: In a 1-L volumetric flask, dissolve 4.79 g dibasic sodium phosphate; 4.59 g monobasic potassium phosphate; 6.43 g sodium chlorate; 1 g ethylenediaminetetraacetic acid, disodium salt, dihydrate in 500 mL of deionized water. Bring to volume with deionized water. Adjust pH to 6.9.
4. L-cysteine, reagent grade.
5. Ethylenediaminetetraacetic acid, disodium salt, dihydrate ($Na_2EDTA•2H_2O$), reagent grade.
6. Sodium phosphate, dibasic, anhydrous (Na_2HPO_4), reagent grade.
7. Potassium phosphate, monobasic, anhydrous (H_2PO_4), reagent grade.
8. Sodium chlorate ($NaClO_3$), reagent grade.
9. Ethylenediaminetetraacetic acid, tetrasodium salt, dihydrate ($Na_4EDTA•2H_2O$)*.
10. Triton-X-100 solution: 1 mL Triton-X-100 plus 50 mL water.
11. Diluting solution: 1% L-cysteine, 3% $Na_4EDTA•2H_2O$ in water. Prepare as follows: Dissolve 10 g of L-cysteine and 30 g of $Na_4EDTA•2H_2O$ in 50 mL of deionized water in a 1-L volumetric flask. Dilute to volume with deionized water. (The pH will be approximately 8.6*.)
12. Calibration stock solution*: Dissolve 10 mg of Maneb in 10 mL diluting solution.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: Plastic bags, polyethylene, 2 quart size, freezer bag type, containing 150-mL hand wash solution.
2. High performance liquid chromatograph (HPLC) with UV detector, 254 nm (or 285 nm if a variable-wavelength UV detector is available). Set chromatograph to conditions on page 3601-1.
3. Ultrasonic water bath.
4. Graduated cylinder to measure water for hand wash 150 mL.
5. Bottles, glass, amber, wide-mouth, 75- to 125-mL, with PTFE-lined screw caps.

SPECIAL PRECAUTIONS: Maneb has degradation products which are known to be carcinogenic, mutagenic, and teratogenic [6-9]. Avoid contact with Maneb by wearing appropriate protective equipment. Na_4EDTA is very alkaline; avoid contact with skin or eyes of either the dry powder or aqueous solutions.

SAMPLING:

NOTE: The sampling procedure has not been thoroughly investigated; this is a prototype method only.

1. Pour 150 mL of water into a plastic bag. Record the total volume of water in the bag.
2. Add 5 drops of Triton-X-100 solution to the water in the bag.
3. Ask the worker to insert his hand into the water and, while holding the bag closed around his arm, shake his hand in the water for approximately 30 seconds.
4. After removing the hand from the bag, add 1 g L-cysteine and 3 g $Na_4EDTA•2H_2O$ to the bag.
   NOTE 1: The EDTA here must be the tetrasodium form, not the disodium form. See SPECIAL PRECAUTIONS.

NOTE 2: Preweighing the L-cysteine and the EDTA into small vials is a convenient way of dispensing these chemicals in the field.

NOTE 3: The addition of EDTA and L-cysteine to the hand-wash solution before washing the hand is not recommended, because these chemicals will make the hand-wash solution very alkaline, slippery, and have an unpleasant odor (from the L-cysteine).

5. Shake the bag until all the L-cysteine and EDTA dissolve.
6. Pour the hand-wash solution from the bag into a 75- to 125-mL amber wide-mouth bottle to overflowing and cap with no headspace.
7. Prepare a blank sample by following all steps above, except step 3.
8. Pack securely for shipment in refrigerant packs to keep at approximately 4 °C, and ship via overnight express.

SAMPLE PREPARATION:

9. On arrival at the laboratory, store the samples at 4 °C.
10. Put capped sample bottles in the ultrasonic bath for 5 to 10 minutes.
11. Transfer 1 to 2 mL of each hand-wash solution, standard, and blank to an autosampler vial for analysis. Analyze within 24 hours. No further sample preparation is necessary.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with at least six working standards over the range of 0.1 to 100 µg/mL.
    a. Pipet aliquots of calibration stock solution into 10-mL volumetric flasks, and bring to volume with diluting solution.
    b. Include a calibration blank of unspiked diluting solution.
    c. Analyze together with field samples, field blanks, and laboratory control samples (steps 14 through 16).
    d. Prepare a calibration graph (peak area vs. concentration, µg/mL).
13. Prepare Laboratory Control Samples (LCS), in duplicate, with each sample set.
    a. Independently prepare quality control Maneb LCS solutions in aqueous 1% L-cysteine, 3% $Na_4EDTA \cdot 2H_2O$ at concentrations within the analytical range.
    b. Analyze along with the field samples, blanks, and liquid standards (steps 14 through 16).

MEASUREMENT:

14. Set liquid chromatograph to manufacturer's recommendations and the parameters given on page 3601-1.
15. Inject sample aliquots (100 µL) manually or with an autosampler. Rinse and dry syringe after each injection.
16. Measure peak areas. If sample peak area exceeds the linear calibration range, dilute with an aqueous 1% L-cysteine, 3% $Na_4EDTA \cdot 2H_2O$ solution, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

17. From the calibration graph, read the concentration, C (µg/mL), of Maneb found in the sample.
18. Calculate the mass of Maneb, M (µg), in the hand wash sample volume, V (mL).

$$M = CxV, \mu g / sample$$

CONFIRMATION:

No confirmation method has been tested. There are several possible alternatives, such as ion-pairing chromatography with a C-18 column [5], or analysis of methylated derivatives on a C-18 column [3,4].

EVALUATION OF METHOD:

This method has been evaluated in the laboratory only. No field samples have been analyzed to date.

LOD/LOQ

A series of liquid standards from 0.1 to 100 µg/mL was prepared in duplicate, analyzed, and fitted with a linear curve. The Limit of Detection (LOD), 0.2 µg/mL, and Limit of Quantitation (LOQ), 0.66 µg/mL, were estimated with the NIOSH SOP 018 method [10].

PRECISION AND ACCURACY

Twenty-four liquid standards were prepared, six at each of four levels: 3xLOQ, 10xLOQ, 30xLOQ, and 100xLOQ. The relative standard deviation of the 100xLOQ level was considerably lower than that of the other three levels and, therefore, was not used to compute the pooled relative standard deviation. The pooled relative standard deviation for the first three levels was 0.015. Since all samples were spiked liquid standards, accuracy and bias were not determined. Since no samples were generated, overall precision was not calculated.

STABILITY

Stability studies were performed on solutions at 6.6 µg/mL Maneb concentration. It was determined that it is necessary to store the samples at 4 °C in a solution of 1% L-cysteine, 3% $Na_4EDTA \cdot 2H_2O$. Samples stored at 4 °C were stable to 30 days with greater than 90% recovery with or without headspace. At 24 °C, however, samples with headspace deteriorated more rapidly. Therefore, as a precaution against the possibility of elevated temperatures during shipping, samples should be stored and shipped with no headspace.

COMMENTS:

Most ethylene-bis-dithiocarbamates (EBDC) containing divalent (or higher) metals, (*e.g.*, Maneb, Mancozeb, and Zineb) dissolve with difficulty in almost every solvent. If the metal ion is removed by complexation with EDTA (at high pH), the EBDC will dissolve but will begin to degrade rapidly, presumably by oxidation, to disulfides or other products. Adding an antioxidant such as L-cysteine greatly inhibits this oxidative degradation. Excluding headspace air has been shown to assist in reducing oxidation; however, cooling to 4 °C is one of the most important factors in sample preservation.

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