Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Diquat

MRID #: 409174-03

Matrix: Water

Analysis: Spectrophotomtr

APPENDIX I

Computer Program

and

Example of Print-out

DISCUSSION

Zero-order absorbance is the recommended routine mode of analysis. In situations where adequate sample cleanup is not obtained, examine the second-derivative results to determine if the better discrimination ability of this technique improves sample analysis.

REFERENCE

(1) Fell, A.F.; Jarvie, D.R.; Stewart, M.J. Clin. Chem., 1981, 27 236.

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CALLULATIONS

1. Zero-Order Absorbance

Correct the absorbance of the sample at the maximum for irrelevant absorption as follows:

(a) Determine correction factors from the two standard readings with the formula

$$K = \frac{A_m^D}{2A_m^D - (A_h^D + A_l^D)}$$

where A_m^D = standard absorbance at the maximum

A_h^D = standard absorbance 4 nm higher than the maximum

A_l^D = standard absorbance 4 nm lower than the maximum.

Average the two k's to give K_{ave}.

(b) The corrected sample absorbance is then given by the formula

$$A_{corr} = K_{ave} \times [2A_m - (A_h + A_l)]$$

where A_m, A_h and A_l are the respective absorbances of the sample.

The ug/ml diquat cation in the sample is then calculated by

$$\mu g/ml = \frac{A_{corr} \times \text{Std (0.5 ug/ml)} \times \text{Dilution Factor} \times 25 \text{ ml}}{A^D_{m(ave)} \times \text{Sample Volume (ml)}}$$

2. Second-Derivative Adsorbance

$$\mu g/ml = \frac{D_L \text{ (sample)} \times 0.5 \text{ ug/ml} \times 25 \text{ ml} \times \text{Dilution Factor}}{\text{Average } D_L \text{(standard)} \times \text{Sample Volume (ml)}}$$

Sodium dithionite solution, 0.2% in 1.0 N NaOH. This reagent is unstable and should not be kept longer than 1.5 hours.

PREPARATION OF SAMPLES

Transfer a 250 ml sample to a 400 ml plastic beaker and adjust to pH 3. The control sample is fortified at this point for recovery purposes. Proceed with the column clean-up.

CLEAN-UP

Place a plug of glass wool in an ion-exchange column and add 4 ml of settled resin in water. Keep the resin covered with water at all times. Use a freshly prepared column for each sample.

Transfer the solution to the column. Using air pressure, percolate the sample through the column at a maximum flow rate of 10 ml per minute. Resettle the resin in the column with approximately 25 ml of water. Wash the column sequentially with another 25 ml deionized water, followed by 25 ml 1/10 saturated ammonium chloride and 50 ml deionized water.

Elute the diquat with saturated ammonium chloride at a flow rate of 1 ml per minute (approximately 10-12 drops per minute). Collect exactly 25 ml of eluate.

MEASUREMENT

Pipet a 10 ml aliquot of the eluate into a test tube. Add 2.0 ml of sodium dithionite solution, mix gently and analyze using the HP 8451A. The instrument is programmed to automatically report both zero-order and second-derivative measurements. For zero-order measurements, values are reported for the peak maximum at 380 nm and at 376 and 384 nm. For second-derivative measurements, values for the peak minimum at 380 nm and the long-wavelength satellite maximum at 388 nm are reported. In addition, the derivative amplitude (D_L) is also reported. Refer to Fell, et. al. (1) for a description of the second-derivative technique. The computer program used to sequence the sample analyses is found in Appendix I along with an example of the print-out of the results. With each set of determinations, analyze two standard solutions containing 0.5 µg/ml diquat cation in saturated NH_4Cl. Prior to each sample measurement, zero the instrument for background by analyzing a reagent blank prepared by mixing 2.0 ml sodium dithionite reagent and 10 ml saturated NH_4Cl.

AQUATIC DISSIPATION STUDIES WITH DIQUAT HERBICIDE

APPENDIX III

ANALYTICAL METHOD RM-5W-4

CHEVRON CHEMICAL COMPANY
AGRICULTURAL CHEMICALS DIVISION
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ANALYSIS OF DIQUAT RESIDUES
IN WATER
METHOD RM-5W-4

FILE NO.: 740.01
DATE: NOVEMBER 16, 1987

INTRODUCTION

Diquat [6, 7-dihydrodipyrido (1, 2-a:2', 1'-c)pyrazidiinium ion], available as the dibromide salt, is a potent herbicide and desiccant, useful for the control of both terrestrial and aquatic weeds and as a pre-harvest desiccant and defoliant. Its use for these purposes requires a sensitive method for determining residues in water.

This revision of RM-5W-3 describes revised ion exchange chromatography parameters. In addition, the concentration of sodium hydroxide was increased from 0.5 to 1.0 N in the reduction procedure. Using a 250 ml sample, the limit of detection is approximately 0.004 µg/ml.

APPARATUS

Plastic Beakers, 400 ml.

Columns, 1x20 cm, equipped with a stopcock and reservoir (a 25 ml burette may be used).

Hewlett Packard 8451A Diode Array Spectrophotometer, HP 9121 Dual Disk Drive and HP 98155A keyboard.

REAGENTS

Sulfuric acid, 18 N.

Ammonium chloride, saturated solution (approximately 5 M).

Cation exchange resin. DOWEX 50W X 8, 200-400 mesh, hydrogen-form (or AG 50W-X8 - analytical grade cation exchange resin available from Bio-Rad Laboratories, Richmond, California). If DOWEX 50W is used, it should be placed in a large chromatography column and back-washed with water to remove fine particles.

Diquat dibromide monohydrate reference standard (50.9% diquat cation), available from Chevron Chemical Company, Ortho Division, Richmond, California.

Stock solution of diquat cation in both water and saturated ammonium chloride. Store in the dark when not in use. These solutions are stable under normal laboratory conditions, but should be protected from direct sunlight.