

PARAQUAT

5003

$C_{12}H_{14}N_2Cl_2$ MW: 257.16 CAS: 4685-14-7 (ion) RTECS: DW1960000 (ion)
 $(C_{12}H_{14}N_2)^{2+}$ (M.W. Paraquat = 186.26)

METHOD: 5003, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984

Issue 2: 15 August 1994

OSHA : 0.5 mg/m³ (skin; respirable)
NIOSH: 0.1 mg/m³ (skin; respirable)
ACGIH: 0.1 mg/m³ (respirable; 0.5 mg/m³ total)

PROPERTIES: (dichloride salt) solid; decomposes @
 300 °C; VP not significant

SYNONYMS: 1,1'-dimethyl-4,4'-bipyridinium dichloride; methyl viologen; CAS # 1910-42-5; 1,1'-dimethyl-4,4'-bipyridinium bis methyl sulfate (CAS #2074-50-2).

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (1-µm PTFE membrane)	TECHNIQUE:	HPLC, UV DETECTION
FLOW RATE:	1 to 4 L/min	ANALYTE:	1,1-dimethyl-4,4'-bipyridium cation
VOL-MIN:	40 L @ 0.5 mg/m ³	DESORPTION:	5 mL water
-MAX:	1000 L	INJECTION VOLUME:	20 µL
SHIPMENT:	routine	MOBILE PHASE:	25% acetonitrile; 75% 0.01 M heptane-sulfonic acid, sodium salt (pH 3.2); 1.5 mL/min
SAMPLE STABILITY:	at least 1 week @ 25 °C	COLUMN:	30 cm x 4-mm ID stainless steel packed with µ-Bondapak C ₁₈ or equivalent
BLANKS:	2 to 10 field blanks per set	DETECTOR:	UV absorption @ 254 nm
ACCURACY		CALIBRATION:	Paraquat dichloride in water
RANGE STUDIED:	0.26 to 1.03 mg/m ³ [1] (90-L samples)	RANGE:	20 to 500 µg/sample [2,3]
BIAS:	- 0.97%	ESTIMATED LOD:	10 µg/sample [2]
OVERALL PRECISION (\hat{S}_{RT}):	0.088 [1]	PRECISION (\hat{S}_r):	0.048 [1]
ACCURACY:	± 17.1%		

APPLICABILITY: The working range is 0.1 to 10 mg/m³ for a 200-L air sample. The paraquat cation is the analyte for this method; therefore, either salt, the dichloride or bismethyl sulfate, can be quantitated. The standards are prepared from a solution of the dichloride salt with appropriate stoichiometric factor applied.

INTERFERENCES: None identified.

OTHER METHODS: This revises Method S294 [2].

REAGENTS:

1. Water, deionized, distilled.
2. Acetonitrile, HPLC grade.
3. 1-Heptanesulfonic acid, sodium salt.
4. Paraquat dichloride.* Dry at 50 °C to remove water of hydration.
5. Calibration stock solution, 0.002 mg paraquat cation/ μL .* Dissolve 27.6 mg anhydrous paraquat dichloride in distilled water to make 10 mL solution. Prepare in duplicate.
6. LC mobile phase, 25% acetonitrile in 0.01 M aqueous 1-heptanesulfonic acid, sodium salt. Add glacial acetic acid to bring pH to 3.2 ± 0.3 .

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 1- μm PTFE filter, 37-mm diameter with backup pad in a two-piece filter cassette held together with tape or shrink bands.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. HPLC, UV absorption detector at 254 nm, integrator and column (page 5003-1).
4. Vials, 20-mL, scintillation.
5. Pipets, 5-mL.
6. Microliter pipets or syringe, 1- to 250- μL .
7. Syringe, 20- μL , or fixed sample loop or autosampler for injections.
8. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Paraquat is listed as a severe poison. Use care in handling [4,5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 40 to 1000 L. Do not exceed 2 mg total dust on filter.

SAMPLE PREPARATION:

3. Carefully transfer the filter from the cassette to a vial using tweezers.
4. Add 5 mL deionized, distilled water to each vial. Cap the vial and gently swirl it to dissolve the sample completely.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards covering the range 10 to 500 μg paraquat per sample.
 - a. Add calibration stock solution with a microliter syringe to 5 mL water in a vial.
 - b. Analyze together with samples and blanks (steps 7 through 9).
 - c. Prepare calibration graph (response vs. μg paraquat).
6. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

7. Set HPLC to conditions given on page 5003-1.
8. Inject sample aliquot using a syringe, a fixed volume sample loop or an autosampler.
9. Measure peak response.

NOTE 1: Retention time under these conditions is ca. 6 to 6.5 min.

NOTE 2: If peak response is above the range of the working standards, dilute with deionized, distilled water, reanalyze, and apply the appropriate dilution factors in calculations.

CALCULATIONS:

10. Read the mass, μg , of Paraquat found on the filter, W , and the average media blank, B , from the calibration graph.
11. Calculate concentration of Paraquat cation, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S294 was issued on March 16, 1979, and validated over the range 0.256 to 1.03 mg/m^3 using a 90-L sample [1,6]. The overall precision, \hat{S}_{r} , was 0.088 with an average recovery of 98.2%, representing a non-significant bias. The concentration of Paraquat in the generation system was verified by an independent method [7]. Recovery was 101% in the range 23.7 to 94.6 μg per sample; another study found 79% recovery of 25 μg per sample and 98% recovery in the range 77 to 463 μg per sample [3]. Collection efficiency of the filter was determined by collecting six filter samples at about 1.8 mg/m^3 for a 90-L sample. The sampler consisted of two filters per cassette arranged so that the back filter was supported by the backup pad and the front filter was separated from the back filter. The overall collection efficiency was 100%. Samples were stored at room temperature for one week and found to be stable.

REFERENCES:

- [1] NIOSH Backup Data Report S294 (unpublished, March, 1979), available as Order No. PB 81-229 684 from NTIS, Springfield, VA 22161.
- [2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5, S294, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
- [3] User check, Wisconsin Occupational Health Laboratory (NIOSH, unpublished, September 27, 1984).
- [4] Criteria for a Recommended Standard...Occupational Exposure to Manufacturing and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978).
- [5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
- [6] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).
- [7] Chevron Chemical Company, Paraquat by Colorimetry, AM-8-1086 (April 7, 1977).

METHOD REVISED BY:

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