HYDROQUINONE 5004

HOC_6H_4OH MW: 110.11 CAS: 123-31-9 RTECS: MX3500000

METHOD: 5004, Issue 3 **EVALUATION:** FULL **Issue 1:** 15 February 1984 **Issue 3:** 26 February 2016

OSHA: 2 mg/m³
NIOSH: C 2 mg/m³/15 min

PROPERTIES: solid; MP 170 °C; BP 285 °C @ 730 mm; VP 0.0024 Pa (1.8 x 10^{-5} mm Hg; 0.11 mg/m³) @ 25 °C

SYNONYMS: 1,4-benzenediol; hydroquinol; quinol; 1,4-dihydroxybenzene

SAMPLING

SAMPLER: FILTER (0.8-µm cellulose ester membrane)

FLOW RATE: 1 - 4 L/min

VOL-MIN: 30 L @ 2 mg/m³
-MAX: 180 L

FIELD TREATMENT: transfer filter immediately to jar with 10 mL 1% acetic acid

SHIPMENT: ship sample solutions

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.8 to 4 mg/m3 [1] (90-L samples)

BIAS: 4.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.061

ACCURACY: ± 15.0%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: hydroquinone

EXTRACTION: 1% acetic acid, 10 mL

INJECTION VOLUME: 100 µL

MOBILE PHASE: 1% acetic acid in H_2O; 1 mL/min

COLUMN: 25 cm x 4.6-mm ID C18/USP L1 column; ambient temperature, 400 to 600 psi (2800-4100 kPa)

DETECTOR: UV @ 290 nm

CALIBRATION: solutions of hydroquinone in 1% aqueous acetic acid

RANGE: 0.06 to 0.8 mg per sample [2]

ESTIMATED LOD: 0.01 mg per sample [3]

PRECISION ($\bar{S}_r$): 0.030 [1]

APPLICABILITY: The working range is 0.7 to 8 mg/m³ for a 90-L air sample or 2 to 25 mg/m³ for a 30-L air sample. This method can be used when significant concentrations of hydroquinone vapor are not present.

INTERFERENCES: None known. Hydroquinone is unstable on the collection media and must be stabilized immediately after collection by dissolution in 1% acetic acid.

OTHER METHODS: This is Method S57 [2] in a revised format. The method also appears in a NIOSH recommended standard [4].

REAGENTS:

1. Hydroquinone, reagent grade.
2. Distilled water.
3. Acetic acid, glacial.
4. Acetic acid, 1%. Dilute 10 mL acetic acid to 1 L with distilled water.
   NOTE: This solution is needed at the sampling site for field treatment of samples.
5. Calibration stock solution, 3.6 mg/mL. Dissolve 0.0900 g hydroquinone in 25 mL 1% acetic acid. Prepare fresh daily, in duplicate.

EQUIPMENT:

1. Sampler: 37-mm cassette containing 0.8-µm cellulose ester membrane filter and cellulose backup pad.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph with UV detector at 290 nm, integrator and column (page 5004-1).
4. Jars, 60-mL, ointment, low form, with PTFE film gaskets and screw caps.
5. Syringe, 100-µL, or autosampler for sample injection.
6. Microliter syringes for standard preparation.
7. Volumetric flasks, 10- and 25-mL, and 1-L.

SPECIAL PRECAUTIONS: None

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 30 to 180 L.
   NOTE: This method will collect hydroquinone aerosol only. The equilibrium vapor pressure is equivalent to 0.11 mg/m^3 at 25 °C and may be a significant factor at elevated temperatures.
3. Immediately after sampling, transfer the filter (do not include backup pad) with tweezers to a 60-mL ointment jar. Add 10 mL 1% acetic acid. Process field blanks similarly.
4. Ship the filters in the ointment jars.

SAMPLE PREPARATION:

5. Transfer the sample solution from the ointment jar to a 25-mL volumetric flask.
6. Rinse the ointment jar twice with 5 mL 1% acetic acid. Add the washings to the volumetric flask. Make up to volume with 1% acetic acid.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.01 to 0.8 mg hydroquinone per sample.
   a. Add known amounts of calibration stock solution to 1% acetic acid in 25-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 9 and 10).
   c. Prepare calibration graph (peak area vs. mg hydroquinone).
   d. Prepare recovery graph (recovery vs. mg hydroquinone).
8. Check recovery with at least three spiked media blanks per sample set.
   a. Add aliquot of calibration stock solution with a microliter syringe directly to a representative filter. Transfer filter to 60-mL ointment jar, add 10 mL 1% acetic acid, and allow to stand overnight.
   b. Prepare and analyze together with working standards (steps 5, 6, 9 and 10).
   c. Calculate recovery [(mg recovered - mg blank)/mg added)].

MEASUREMENT:

9. Set HPLC to conditions given on page 5004-1. Inject 100-µL sample aliquot.

10. Measure peak area. Retention time is ca. 5.2 min under these conditions.

CALCULATIONS:

11. Determine the mass, mg (corrected for recovery) of hydroquinone, found in the sample (W) and in the average media blank (B).
12. Calculate concentration of hydroquinone, C, in the air volume sampled, V (L):

$$C = \frac{(W - B)x10^3}{V}, mg/m^3$$

EVALUATION OF METHOD:

Method S57 [2] was issued on November 26, 1976, and validated over the range 0.8 to 4 mg/m^3 at 20 °C and 762 mm Hg using 90-L air samples [1,5]. Overall precision, $\hat{\mathbf{S}}_{\mathbf{rT}}$, was 0.061 with average recovery 105%, representing a non-significant bias. The atmospheres were generated by atomization of an aqueous solution of hydroquinone into dry air; aerosol concentrations were independently verified by direct UV spectrophotometry on filter samples. Average collection efficiency was 100% at 4 mg/m^3. No loss of hydroquinone was seen from filters spiked with 720 µg hydroquinone, and then used to sample 180 L clean air, indicating the hydroquinone vapor pressure is not significant at these conditions. At elevated temperature, however, contribution from vapor may be significant. Storage studies were conducted by storing exposed filters in 1% acetic acid at ambient temperature for seven days. No change in hydroquinone concentration was seen.

REFERENCES:

[1] NIOSH [1976]. Backup data report No. S57. In: Ten NIOSH analytical methods, set 2. Unpublished. Available as Order No. PB 271-464, from NTIS, Springfield, VA.

[2] NIOSH [1977]. Hydroquinone: Method S57. In: Taylor DG, ed. NIOSH manual of analytical methods. 2nd ed. (vol 2) Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-157-B.

[3] A.D. Little, Inc. [1983]. User check. NIOSH Sequence #4121Q. Unpublished.

[4] NIOSH [1978]. Criteria for a recommended standard-occupational exposure to hydroquinone. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 78-155.

[5] NIOSH [1980]. NIOSH research report-development and validation of methods for sampling and analysis of workplace toxic substances. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 80-133.

METHOD REVISED BY:

Jerome Smith, Ph.D., NIOSH; S57 originally validated under NIOSH Contract 210-76-0123.